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## Task-specific thioglycolate ionic liquids for heavy metal extraction: Synthesis, extraction efficacies and recycling properties

Sonja Platzer<sup>a</sup>, Mega Kar<sup>b</sup>, Raphlin Leyma<sup>a</sup>, Sonia Chib<sup>a</sup>, Alexander Roller<sup>a</sup>, Franz Jirsa<sup>a,c</sup>, Regina Krachler<sup>a</sup>, Douglas R. MacFarlane<sup>b</sup>, Wolfgang Kandioller<sup>a,\*</sup>, Bernhard K. Keppler<sup>a</sup>

<sup>a</sup> Institute of Inorganic Chemistry, Faculty of Chemistry, University of Vienna, Waehringer Str. 42, 1090 Vienna, Austria

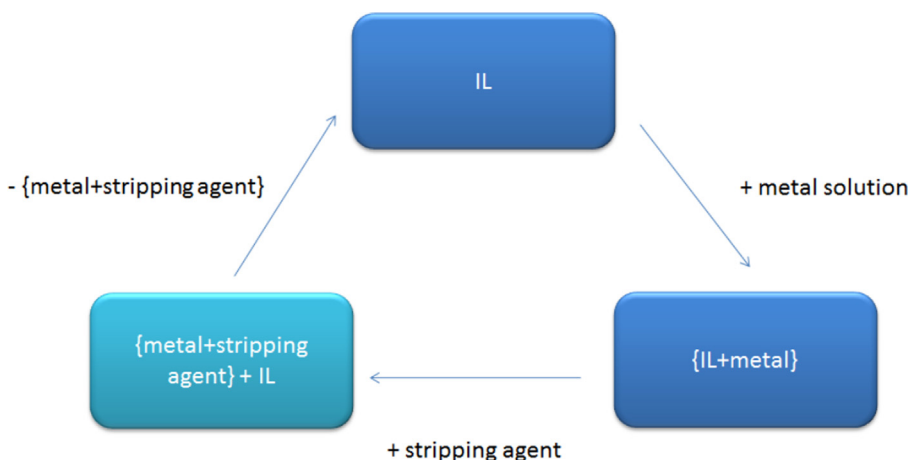
<sup>b</sup> School of Chemistry, Monash University, Clayton, Victoria 3800, Australia

<sup>c</sup> Department of Zoology, University of Johannesburg, PO Box 524, Auckland Park, 2006 Johannesburg, South Africa

### HIGHLIGHTS

- Thioglycolate-based ionic liquids have been synthesized and their physicochemical properties have been examined.
- The developed ionic liquids can efficiently remove Cu(II) and Cd(II).
- Loaded ionic liquids can be recycled by application of different stripping protocols.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Eight novel task-specific ionic liquids (TSILs) based on the thioglycolate anion designed for heavy metal extraction have been prepared and characterized by <sup>1</sup>H and <sup>13</sup>C NMR, UV-Vis, infrared, ESI-MS, conductivity, viscosity, density and thermal properties. Evaluation of their time-resolved extraction abilities towards cadmium(II) and copper(II) in aqueous solutions have been investigated where distribution ratios up to 1200 were observed. For elucidation of the IL extraction mode, crystals were grown where Cd(II) was converted with an excess of S-butyl thioglycolate. It was found by X-ray diffraction analysis that cadmium is coordinated by five oxygen and one sulfur donor atoms provided by two thioglycolate molecules and one water molecule. Leaching behavior of the hydrophobic ionic liquids into aqueous systems was studied by TOC (total dissolved organic carbon) measurements. Additionally, the immobilization on polypropylene was elucidated and revealed slower metal extraction rates and similar leaching behavior. Finally, recovery processes for cadmium and copper after extraction were performed and recyclability was successfully proven for both metals.

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\* Corresponding author.

E-mail address: [wolfgang.kandioller@univie.ac.at](mailto:wolfgang.kandioller@univie.ac.at) (W. Kandioller).

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## 1. Introduction

Heavy metal pollution is among the world's most alarming environmental problems whereby more than 95 million people are affected. The top six toxicants in 2015 were lead, radionuclides, mercury, hexavalent chromium, pesticides and cadmium [1]. The European Water Framework Directive lists certain heavy metals (e.g. cadmium, lead, mercury) and their compounds as “priority” substances [2], where excess exposure may result in toxicity. Therefore, finding selective, cost-efficient and eco-friendly metal extracting compounds is of great interest worldwide. Heavy metals can be removed from aqueous solution by chemical precipitation, flotation, adsorption, ion exchange and electrochemical deposition. Chemical precipitation is the most widely used, yielding insoluble metal hydroxides [3]; however, the major drawback of this simple and cost-effective approach is the formation of a toxic sludge. Another method for waste water purification is liquid-liquid extraction which can be applied in a range of different applications [4–7]. Recently, ionic liquids (ILs) have shown good performance as an extractant phase in the separation of heavy metal ions [8–11]. ILs are low melting point salts, mostly achieved by use of bulky asymmetric cations and weakly coordinating anions [12]. These compounds have attracted much attention from research teams due to their characteristic properties: low vapor pressure, high thermal and (electro-)chemical stability and in the liquid state over a broad temperature range. Tailoring the length and branching of the alkyl chains and the anionic precursor can be used to produce “designer solvents” for task-specific applications including metal extraction [13]. Nonetheless, metal extracting agents have to be low cost and recyclable. On one hand, metals should be stripped off selectively and on the other hand, back-extraction agents (e.g. nitric acid) should not destroy the TSILs. Several examples of back-extraction agents are under investigation for different heavy metal ions [14–16].

ILs containing thioglycolic acid derivatives have been used for hydrogen peroxide reduction [17], for deoxyribonucleic acid biosensors [18] and in preparation of CdTe quantum dots [19]. Vijavaraghavan *et al.* have investigated water soluble thioglycolates-based ILs as alternatives for sodium sulfide-free leather production [20]. As reported by Wang [21], ammonium thioglycolate-functionalized eggshell membrane showed high potential as a column packing for waste water purification. Furthermore, mercury(II), lead(II) and silver(I) salts have been removed quantitatively by thiol functionalized magnetic mesoporous silica from different water matrices [22]. Recognizing that thioglycolates show affinity towards binding of soft metal ions, we hypothesized that they could be used as part of hydrophobic, task-specific ILs for metal ion extraction from waste waters. We demonstrate the use of the extraction process with cadmium and copper.

Cadmium can be generated from heavy metal mining, industries and metallurgy where nickel-cadmium batteries are widely used. Since 2011, the European Commission banned the usage of cadmium in jewelry, polyvinylchloride and alloys for brazing [23]. Exposure to cadmium has shown severe effects on human and animal health including chemical pneumonitis, bone deformation and kidney damage [24]. Copper was chosen as a typical 3d metal ion for study in this work. It is thought to be genotoxic at high concentrations [25].

Thus, we report here the synthesis of eight TSILs based on thioglycolic acid designed for the heavy metal extraction (Fig. 1). These TSILs bearing thioether anions are evaluated by liquid-liquid and liquid-solid extraction (immobilized ILs on polypropylene hollow fibers) for their cadmium and copper extraction efficacy.

## 2. Experimental

### 2.1. Materials

Benzyl bromide (98%), thioglycolic acid ( $\geq 98\%$ ), 1-iodopentane (98%), 1-iodobutane (99%), 1-iodohexane ( $>98\%$ ), NaOH (p.a.), EDTA-2H<sub>2</sub>O (disodium salt, 99+%) and standard solutions of Cd and Cu (1000 mg L<sup>-1</sup> in 2% (w/w) HNO<sub>3</sub>) for atomic absorption spectroscopy for the instrument calibration and extraction experiments were purchased from Sigma Aldrich. Potassium hydroxide (p.a.) and CdCl<sub>2</sub>·2H<sub>2</sub>O were obtained from Merck. HNO<sub>3</sub> (trace select,  $\geq 69\%$ ), HCl (37%), KHCO<sub>3</sub> (p.a.) and CaCl<sub>2</sub>·2H<sub>2</sub>O (p.a.) were purchased from Fluka and NaOH (50%) from J. T. Baker. Benzyl bromide was distilled under reduced pressure before using. Methyltriocetylphosphonium methylcarbonate (99%) ([TOMP][MC]) and methyltriocetylammmonium methylcarbonate (99%) ([TOMA][MC]) were purchased from proionic (Austria). Utilized solvents were of HPLC grade and used without further purification. Immobilization studies were conducted using polypropylene Accurel PP S6/2 capillary hollow fibers membranes with an 1800  $\mu$ m internal diameter (75% porosity and 0.2  $\mu$ m pore size) obtained from Membrana (Germany).

### 2.2. Synthesis

Eight ionic liquids (Fig. 1), namely methyltriocetylammmonium butylsulfanyl acetate [N<sub>1888</sub>][C<sub>4</sub>SAC], methyltriocetylammmonium pentylsulfanyl acetate [N<sub>1888</sub>][C<sub>5</sub>SAC], methyltriocetylammmonium hexylsulfanyl acetate [N<sub>1888</sub>][C<sub>6</sub>SAC], methyltriocetylammmonium benzylsulfanyl acetate [N<sub>1888</sub>][BnSAC], methyltriocetylphosphonium butylsulfanyl acetate [P<sub>1888</sub>][C<sub>4</sub>SAC], methyltriocetylphosphonium pentylsulfanyl acetate [P<sub>1888</sub>][C<sub>5</sub>SAC], methyltriocetylphosphonium hexylsulfanyl acetate [P<sub>1888</sub>][C<sub>6</sub>SAC] and methyltriocetylphosphonium benzylsulfanyl acetate [P<sub>1888</sub>][BnSAC], were synthesized in two steps [26] and detailed protocols and characterization of the obtained products are provided in the Supplementary information.

### 2.3. Analysis

<sup>1</sup>H and <sup>13</sup>C NMR spectra were carried out on a Bruker 400 MHz spectrometer. Low resolution ESI mass spectra were recorded on a Waters micromass ZQ QMS connected to an Agilent 1200 series, using methanol as solvent. Density measurements were conducted on an Anton Paar DMA 500 density meter using the ‘oscillating U-tube principle’. FT-IR spectra were conducted on a Bruker Vertex 70 Fourier transform IR spectrometer. Viscosities were measured on an Anton Paar Lovis 2000 M microviscometer by using the falling ball technique. Conductivity measurements were performed on a solartron SI 1260 AC impedance/gain-phase analyzer from 0.1 Hz to 10 MHz. DSC measurements were carried out on a DSC Q 100 instrument with a scan rate of 10 °C min<sup>-1</sup>. All prepared samples for the water content measurements were dried at 40 °C under reduced pressure for 24 h and finally measured using a Metrohm 831 KF coulometer.

### 2.4. Experimental extraction studies

100 mg of the IL (water saturated) was shaken with 5 mL 0.1 M CaCl<sub>2</sub> metal-containing solution (initial pH 7; 2 ppm Cd or 5 ppm Cu) for 15 min, 30 min, 1 h and 2 h at 300 rpm at 20 °C. Afterwards, aqueous phases were analyzed by using a Perkin Elmer AAnalyst 200 flame atomic absorption spectrometer (F-AAS) for Cd and Cu (wavelengths: Cd 228.8 nm, Cu 324.8 nm) via external standard calibration in a working range of 0.01–5.00 mg L<sup>-1</sup>. The F-AAS detection limits were 0.1 mg L<sup>-1</sup> for Cd and 0.5 mg L<sup>-1</sup> for Cu, with

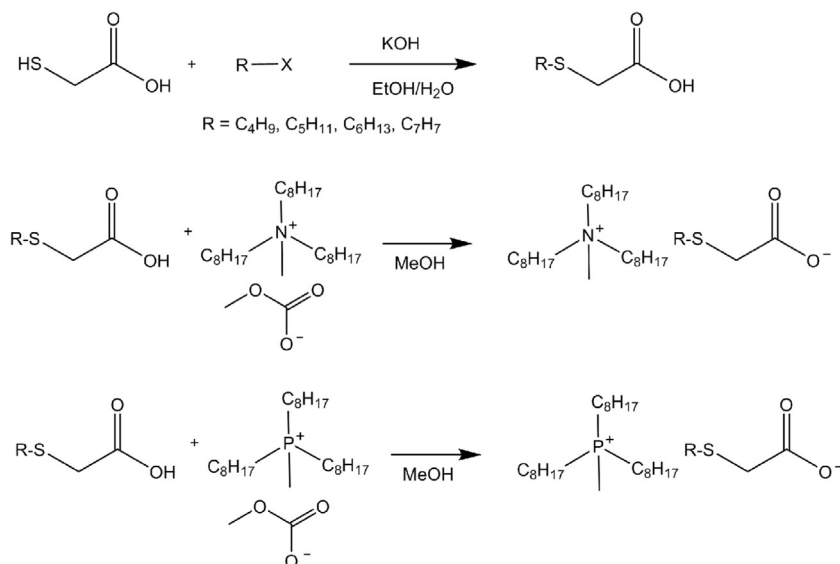


Fig. 1. Synthetic pathway of novel TSILs.

an uncertainty of max. 5%. All extraction experiments were performed at least in triplicates with satisfying agreement. For the extraction mechanism, the Cd-loaded IL was analyzed by FT-IR measurement.

Extraction efficiencies (E) were calculated from Eq. (1):

$$E(\%) = \frac{c_{0,\text{aq}} - c_{1,\text{aq}}}{c_{0,\text{aq}}} * 100 \quad (1)$$

where  $c_{0,\text{aq}}$  and  $c_{1,\text{aq}}$  are the total metal concentrations before and after the extraction in the aqueous phase, respectively.

Distribution ratios (D) can be empirically determined from Eq. (2) as follows

$$D = \frac{(c_{0,\text{aq}} - c_{1,\text{aq}}) * m_{\text{W}}}{c_{1,\text{aq}} * m_{\text{IL}}} \quad (2)$$

where  $c_{0,\text{aq}}$  and  $c_{1,\text{aq}}$  are the total metal concentrations before and after the extraction in the aqueous phase with  $m_{\text{W}}$  and  $m_{\text{IL}}$  being the mass of water and IL used for the extraction, respectively. Maximum observable D values for Cd is 950 and 1200 for Cu, correspondingly.

## 2.5. Leaching measurements

Throughout this manuscript, the word “leaching” is used for the loss of the IL into the aqueous phase. Leaching of the ILs into the water phase was tested in the following way: 100 mg of IL was shaken with 0.1 M  $\text{CaCl}_2$  aqueous solution (5 mL) for 2 h. 3 mL of the aqueous solution was diluted with 9 mL double distilled water. The dependence of the leaching into the aqueous phase on the ionic strength is well known [27] so all experiments were performed with 0.1 M  $\text{CaCl}_2$  solution. The samples were acidified to  $\text{pH} \approx 2$  with HCl and purged with carrier gas for 5 min prior to combustion in the TOC analyzer and the total organic carbon in the diluted aqueous phase sample (in  $\text{mg carbon L}^{-1}$  and leaching percentage) was determined by three independent experiments (Table 1). Respective leaching percentages (Eq. (3)) are calculated as follows:

$$\text{leaching (mg)} = \frac{\text{TOC} * V_{\text{sample}}}{V_{\text{total}}} * V_{\text{sample}} * C_{\text{IL}} \quad (3)$$

TOC is the measured amount of  $\text{mg carbon L}^{-1}$ ,  $V_{\text{sample}}$  and  $V_{\text{total}}$  are the volumes taken for the leaching measurement and  $C_{\text{IL}}$  the carbon content per IL in%.

## 2.6. Halide impurities measurements

The bromide and iodide contents were determined by dissolving the ILs in ethanol/water (1:1). The solution was then analyzed using capillary electrophoresis (CRYSTAL 310) with a conductivity detector (TraceDec).

## 2.7. Walden plots

For determination of the ionicities of the ILs, Walden plots have been designed after the Walden rule (Eq. (4)) where [28]:

$$k = \Lambda \eta \quad (4)$$

$\Lambda$  is the molar conductivity,  $\eta$  represents the viscosity, depending on the temperature dependent constant (k).

## 2.8. Back-extraction experiments

Two different procedures for back-extraction the metals have been applied in this work. Firstly, the IL ( $[\text{N}_{1888}][\text{C}_6\text{SAC}]$ , 100 mg) was shaken with 0.1 M  $\text{CaCl}_2$  (5 mL) metal-containing solution for 30 min in the case of Cd (2 ppm) and 1 h for Cu (5 ppm) at 300 rpm. After this extraction, the IL was separated and the metal back-extracted into the aqueous solution by shaking with either 5 mL of 0.5 M  $\text{HNO}_3$ , 0.5 M ETDA ( $\text{pH} 7$ ) or 0.5 M HCl for 60 min at 300 rpm. After separation, the aqueous solution was analyzed by F-AAS.

Secondly,  $[\text{N}_{1888}][\text{C}_6\text{SAC}]$  (100 mg) was shaken with 0.1 M  $\text{CaCl}_2$  (5 mL)  $\text{Cu}^{2+}$  solution (5 ppm) for 1 h at 300 rpm. After separation, 1 M  $\text{HNO}_3$  (5 mL) was added to the IL and shaken for 1 h at 300 rpm. The IL was separated and treated with sat.  $\text{KHCO}_3$  solution (5 mL) for 10 min at 300 rpm and both aqueous phases were analyzed by F-AAS.

For each cycle, fresh metal and stripping solutions were used. These procedures were performed five times with three independent experiments. The back-extraction efficacy (S, Eq. (5)) was calculated as

$$S(\%) = \frac{c_0 - c_{\text{IL}}}{c_0} * 100 \quad (5)$$

where  $c_0$  is the initial metal concentration in the IL phase before back-extraction and  $c_{\text{IL}}$  is the metal concentration in the IL phase after back-extraction.

**Table 1**  
Physicochemical properties of thioglycolate-based ionic liquids.

ionic liquid	physical appearance at room temperature	density [g cm <sup>-3</sup> ] <sup>a</sup>	viscosity [P] <sup>a</sup>	conductivity [S cm <sup>-1</sup> ] <sup>a</sup>	leaching (%) <sup>b</sup>	Br <sup>-</sup> (%)	I <sup>-</sup> (%)	H <sub>2</sub> O content (neat) (%)	H <sub>2</sub> O content (water sat.) (%)
[N <sub>1888</sub> ][C <sub>4</sub> SAC]	white solid	0.90	9.41	3.74·10 <sup>-5</sup>	1.1	–	<0.1	–	3.20
[N <sub>1888</sub> ][C <sub>5</sub> SAC]	beige solid	0.91	10.67	3.06·10 <sup>-5</sup>	0.5 ± 0.1	–	<0.1	–	3.84
[N <sub>1888</sub> ][C <sub>6</sub> SAC]	slightly yellow solid	0.91	11.90	2.48·10 <sup>-5</sup>	0.3 ± 0.1	–	0.1	–	5.35
[N <sub>1888</sub> ][BnSAC]	orange oil	0.94	–	2.60·10 <sup>-5</sup>	0.8	<0.1	–	0.48	3.40
[P <sub>1888</sub> ][C <sub>4</sub> SAC]	slightly pink solid	0.93	4.97	1.21·10 <sup>-4</sup>	1.2	–	<0.1	–	4.24
[P <sub>1888</sub> ][C <sub>5</sub> SAC]	white solid	0.92	4.47	1.51·10 <sup>-4</sup>	0.8	–	0.1	–	6.30
[P <sub>1888</sub> ][C <sub>6</sub> SAC]	slightly yellow solid	0.93	4.84	1.43·10 <sup>-4</sup>	0.4	–	0.1	–	6.14
[P <sub>1888</sub> ][BnSAC]	yellow oil	0.96	11.23	1.89·10 <sup>-5</sup>	1.0	<0.1	–	0.34	1.15

<sup>a</sup> Water-saturated IL measured at 25 °C (±5%).<sup>b</sup> Measured after 2 h at 25 °C.

### 2.9. Immobilization of ionic liquids in polypropylene hollow fibers and extraction

Polypropylene hollow fibers were prepared similar to literature methods [29]. About 100 mg of the IL was filled in 2.7 cm polypropylene hollow fibers with a syringe. The membrane was sealed using hot glue (Rothenberger Industrial GmbH, Germany). The fibers were shaken with metal solutions (5 mL, pH 7, 0.1 M CaCl<sub>2</sub>) for 2 h and 6 h at 300 rpm. After separation, 1 mL of the aqueous phase was diluted with distilled water (to 10 mL) and leaching was determined by TOC measurement as follows (Eq. (6))

$$\text{leaching (mg)} = \frac{\text{TOC}}{V_{\text{total}}} \cdot C_{\text{IL}} \quad (6)$$

where TOC is the quantified total carbon/L,  $V_{\text{total}}$  is the dilution volume and  $C_{\text{IL}}$  being the carbon content/IL.

The remaining metal concentration was determined by F-AAS in triplicate (at least).

## 3. Results and discussion

### 3.1. Synthesis and characterization

Within this project a series of thioglycolate-based ILs were synthesized. The first step was the alkylation of the free thiol group of thioglycolic acid with alkyl halides, which was achieved in very good yields (Fig. 1). One standard method for the synthesis of ILs is anion-metathesis; however, side products such as inorganic salts are formed during the reaction and therefore purification steps are necessary to isolate the desired products [30], as can be seen in the case of [N<sub>1888</sub>][Cl] and [P<sub>6614</sub>][Cl], where more than 1 wt% chloride can be detected after work up [31]. A straight-forward and “greener” approach to avoid such inorganic impurities and facilitate the purification process is the utilization of the respective methyltrioctylammonium and methyltrioctylphosphonium methyl carbonates. Due to this experimental modification only methanol and carbon dioxide are formed as side products and therefore it provides an elegant way to produce large amounts of highly pure ILs in quantitative yields. The improved synthetic protocol provides a cheap and efficient method for task-specific ILs from commercially available starting materials. Overall, eight novel ILs have been isolated in sufficient purity and characterized by standard analytical methods.

NMR experiments revealed that proton signals of SCH<sub>2</sub>COO<sup>-</sup> were slightly shifted upfield from 3.25 to 3.21 ppm compared to the respective carboxylic acids. The cations of the aliphatic groups could not be unambiguously assigned due to overlapping of the peaks. The pK<sub>a</sub> values of the investigated anion were reported between 3.708 and 3.758, where inductive effects decrease the acid strengths [26]. The presence of halide impurities (iodide in the case

for all [C<sub>4</sub>SAC], [C<sub>5</sub>SAC] and [C<sub>6</sub>SAC]-based ILs and bromide for all [BnSAC]-based ones) are given in Table 1. Highest halide impurities were found for [N<sub>1888</sub>][C<sub>5</sub>SAC], [P<sub>1888</sub>][C<sub>5</sub>SAC] and [P<sub>1888</sub>][C<sub>6</sub>SAC] with 0.1 % iodide, respectively (Table 1). Applying this improved synthetic strategy, the halide content is significantly lower compared to reported TSILs suitable for heavy metal extraction [32].

### 3.2. Physicochemical properties

The application of ILs for liquid-liquid extraction is strongly dependent on their physicochemical properties and the respective data is summarized in Table 1. All eight ILs possess densities less than 1 g cm<sup>-3</sup> and show deliquescent behavior. Water-saturated ILs (up to 6.3 wt% water) yielded higher fluidity compared to pure ILs, which were present as extremely viscous to semi-solid substances. The synthesized thioglycolate-based [N<sub>1888</sub>]<sup>+</sup> and [P<sub>1888</sub>]<sup>+</sup> ILs possess higher fluidities compared to reported ammonium and phosphonium ILs designed for metal extraction or [N<sub>1888</sub>][Cl] [32]. The density data revealed that the S-benzyl derived ILs have the highest density among this group of ILs. It is evident that the phosphonium-based ILs exhibit slightly higher densities than their ammonium counterparts. This is in contrast to the observation of Carvalho *et al.* where higher densities were found for ammonium ILs compared to the respective phosphonium analogs, which was explained by the more rigid structure of ammonium ILs [33]. After water-saturation of the thioglycolate ILs an increase in density was observed. The synthesized ILs are air stable and soluble in common organic solvents, but insoluble in water. Miscibilities were visually determined by adding each solvent to small amounts of the ILs and the obtained results are presented in Table S1.

Melting points of the salts tend to decrease with increasing size of cation and anion and were found between 22 and 48 °C (Table S2). The highest melting points were found for neat pentylsulfanyl acetate. This observation might be explained by more efficient packing of the ions in the crystal lattice. By comparing the melting points of the phosphonium-based ILs, the water saturated ILs were found to melt at lower temperature than their neat analogs. [N<sub>1888</sub>][BnSAC] and [P<sub>1888</sub>][BnSAC] were found to be liquid at room temperature and their glass transition temperatures, where a transition from solid state to amorphous solid takes place, are represented in Table S3. Bigger cations lead to higher steric hindrance and less ionic mobility, which results in higher glass transition temperature. For these ILs, the glass transition temperature is decreasing with increasing water content which is well reported for these mixtures [34].

ILs are ion conductors and their conductivities depend on the size of the ions, the viscosity and the temperature. It was found that the determined conductivities (see Table 1) are in the same range as [N<sub>1888</sub>][Cl] (2.6·10<sup>-5</sup> S cm<sup>-1</sup> at 298 K) [35,36]. Conductivities of the phosphonium ILs were found to

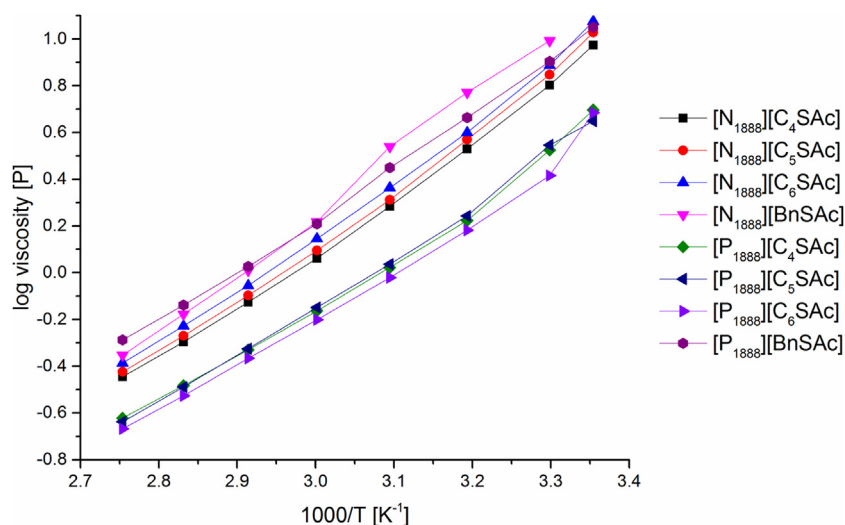


Fig. 2. Viscosities of the water-saturated ionic liquids as a function of reciprocal temperature.

be higher compared to the ammonium analogues and the highest conductivity of the phosphonium-based ILs is found for the pentyl derivative  $[P_{1888}][C_5SAC]$  ( $1.51 \cdot 10^{-4} \text{ S cm}^{-1}$ ). The conductivity decreases with increasing chain length for the ammonium ILs:  $[N_{1888}][C_4SAC] > [N_{1888}][C_5SAC] > [N_{1888}][C_6SAC]$ , which could be explained by increasing viscosity. As shown in Table 1, the  $[P_{1888}]$  ILs are more fluid than the methyltrioctylammonium ones. The decrease of the viscosity at higher temperature is much higher for the more viscous ILs, e.g.  $[N_{1888}][BnSAC]$  and  $[P_{1888}][BnSAC]$ , which is in accordance with the literature (Fig. 2) [37]. According to Fig. 2, phosphonium IL possess smaller activation barriers for diffusion, but there is no clear trend with regard to the chain length.

Although ILs entirely consist of ions, ion association can influence their properties including their transport and solvency properties. The temperature-depending correlation between the molar conductivity to its viscosity of the synthesized ILs is shown in Fig. 3 in the form of a Walden plot. The 0.01 M KCl solution line represents an ideal case where the ions are thought to move independently. Above this line, ILs are considered to be “super ILs”. The range between 0.01 M KCl and the 10% ionization line represents “good IL” with regard to its ionicity where the movement of the ions is partly correlated [38]. Neat  $[P_{1888}][BnSAC]$  was found to sit below the 10% ionization level which indicates only low ionicity.  $[P_{1888}][C_4SAC]$ ,  $[P_{1888}][C_5SAC]$  and  $[P_{1888}][C_6SAC]$  showed similar ionicities between the 0.01 M KCl and the 10% KCl ionization lines.

The low ionicity of neat  $[N_{1888}][BnSAC]$  in Fig. 4 can be explained by its high viscosity and hence hindered ion movement suggesting more ion pairs or ion aggregates. Nevertheless, all  $[N_{1888}]^+$  ILs show relatively similar ionicities. In general, low molar conductivities of the synthesized ILs might be due to the size of the cation (long alkyl chains) and their low fluidity. In the presence of water, the viscosity of the S-benzyl acetate decreases and the ion movement is better facilitated. Overall the phosphonium-based ILs show higher ionicity than the ammonium analogues. By comparing saturated and neat ILs, the presence of water slightly increases ionicity as might be expected due to disruption of ion associations by water molecules.

In the Arrhenius plot of conductivity (Fig. S1), the temperature dependence of the conductivity of  $[P_{1888}]^+$  ILs is displayed. Overall, the investigated ILs follow Arrhenius behavior with a non-linear correlation between temperature and conductivity which is in good accordance to reported phosphonium-based ILs [38].  $[P_{1888}][C_5SAC]$  is the most fluid representative of the  $[P_{1888}]$  ILs with additionally the highest conductivity.

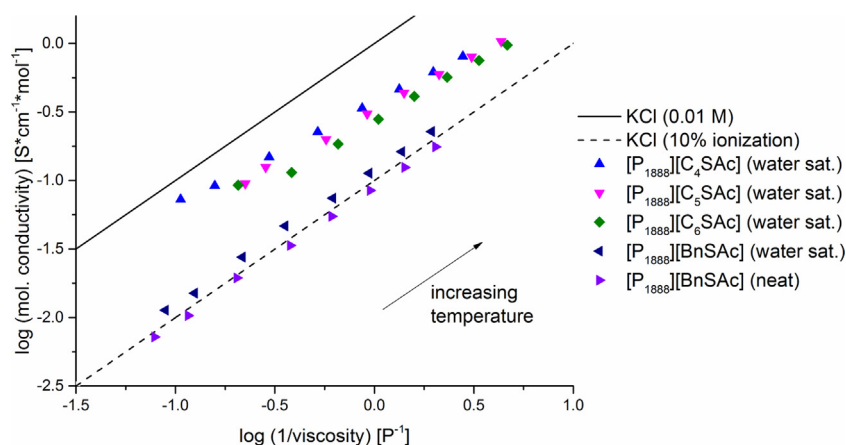
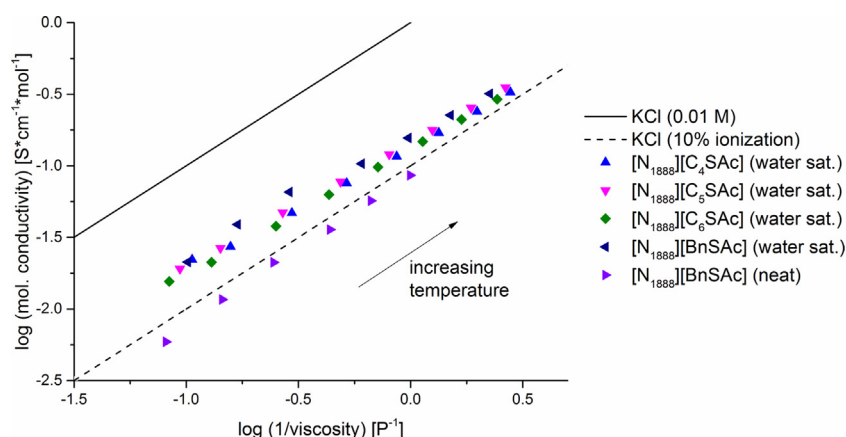
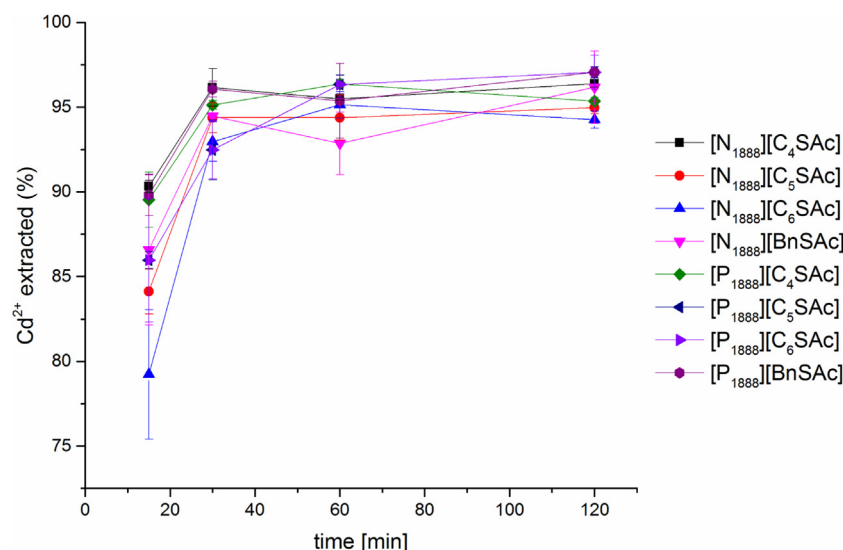
### 3.3. Leaching experiments

For successful application of ILs as extracting agents, low aqueous solubility to minimize the loss into the aqueous phase is required [39]. This process is known as “leaching”. During a liquid-liquid extraction process, the IL can partly dissolve in the aqueous phase and contaminate it. For determination of the IL solubility in water, different methods are common such as quantitative  $^1\text{H}$  NMR [40] or TOC measurements [41]. The experimental data represented in Table 1, less than 1.2% leached after 2 h under the reported conditions considering that  $[C_xSAC]^- = [N_{1888}]^+$  or  $[P_{1888}]^+$  in the aqueous phase and the lowest leaching values are found for the hexylsulfanyl acetate-based ILs. Overall, there is a good match between the chain length of the anion and leaching into the aqueous phase. The ammonium-based ILs showed less leaching than their phosphonium counterparts.

### 3.4. Extraction studies

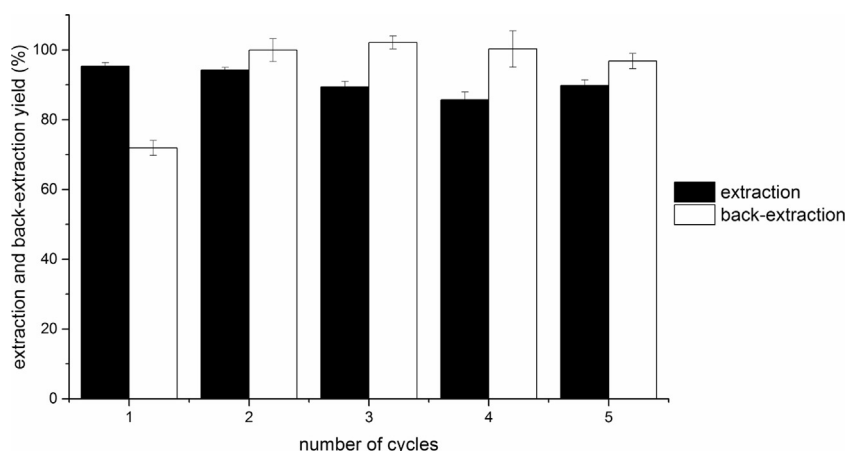
One requirement for ILs as extracting agents is the efficient removal of metal ions which can be manipulated by proper selection of the anion. For this reason, we chose thioglycolates as simple and effective anions with well-known binding characteristics for metal ions. Using these task-specific ILs, no organic solvent or additional extracting agents are needed. As the neat salts exhibit high viscosities lower the mass transfer rate, we worked only with the water-saturated salts, which rendered them liquid at r.t. in all cases (Fig. 7). For the metal extractions, we chose a constant ionic strength at 0.1 M  $\text{CaCl}_2$  in accordance with previous experimental setups [42,43]. As it can be seen in Figs. 5 and S2 all eight ILs show high affinity towards cadmium and copper. Within 30 min, more than 90% of the cadmium was extracted with all ILs from the aqueous phase. As a result of the time-dependent cadmium extraction, this study demonstrates no significant difference between  $[N_{1888}]^+$  and  $[P_{1888}]^+$  ILs.

The extraction mechanism of these TSILs was investigated to elucidate the binding mode of cadmium with the chelating anions of the IL. Therefore  $C_4SACH$  was reacted with  $\text{Cd(II)}$  yielding single crystals suitable for X-ray diffraction analysis; however, the quality of the obtained crystal was insufficient for the CCDC database (synthesis, crystal data, data collection parameters and structure refinement details are given in the Supplementary information). Nevertheless the potential binding mode of cadmium could be elucidated by the measured data; the obtained solid-state struc-

Fig. 3. Walden plot for  $[P_{1888}]^+$  ILs.Fig. 4. Walden plot for  $[N_{1888}]^+$  ILs.Fig. 5. Time-dependent extraction efficiencies for cadmium (100 mg IL, 5 mL Cd stock solution (2 ppm), 0.1 M  $CaCl_2$ , pH 7).

ture demonstrated that cadmium is surrounded by five oxygen atoms and one sulfur atom provided by two thioglycolates and one water molecule (Fig. S6 and S7). However, additional FT-IR measurements of loaded IL from extraction experiments utilizing  $CdCl_2$  revealed that the carbonyl signals from  $[N_{1888}][C_6SAC]$  at  $1597\text{ cm}^{-1}$  and  $[P_{1888}][C_6SAC]$  at  $1589\text{ cm}^{-1}$  decreased and shifted

to  $1639\text{ cm}^{-1}$ . The peaks at  $1359$  and  $1207\text{ cm}^{-1}$ , which can be clearly assigned to the thioglycolate derivative in  $[N_{1888}][C_6SAC]$ , behaved similarly upon treatment with cadmium(II). Far infrared (FIR) investigations clearly indicated Cd–Cl vibrational bands at  $247\text{ cm}^{-1}$  for  $[N_{1888}][C_6SAC]$  and  $250\text{ cm}^{-1}$  for  $[P_{1888}][C_6SAC]$  (Fig. S5). This is in good accordance to other reported metal-halogen



**Fig. 6.**  $\text{Cd}^{2+}$  extraction and back-extraction percentages for  $[\text{N}_{1888}][\text{C}_6\text{SAC}]$  with 0.5 M  $\text{HNO}_3$ . Percentage of back-extraction is referred to the amount of cadmium in the IL.

**Table 2**

Distribution ratios  $D$  for  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  after 120 min at pH 7 (initial)  $\pm 5\%$ , based on 100 mg IL and 5 mL metal-containing solution.

	$D_{\text{Cd}}$	$D_{\text{Cu}}$
$[\text{N}_{1888}][\text{C}_4\text{SAC}]$	950	144
$[\text{N}_{1888}][\text{C}_5\text{SAC}]$	943	721
$[\text{N}_{1888}][\text{C}_6\text{SAC}]$	820	1200
$[\text{N}_{1888}][\text{BnSAC}]$	731	849
$[\text{P}_{1888}][\text{C}_4\text{SAC}]$	950	882
$[\text{P}_{1888}][\text{C}_5\text{SAC}]$	950	1200
$[\text{P}_{1888}][\text{C}_6\text{SAC}]$	950	1200
$[\text{P}_{1888}][\text{BnSAC}]$	950	1045

vibrations [44]. These observations support a coordination of cadmium to the thioglycolate as well as an uptake of chloride into the IL.

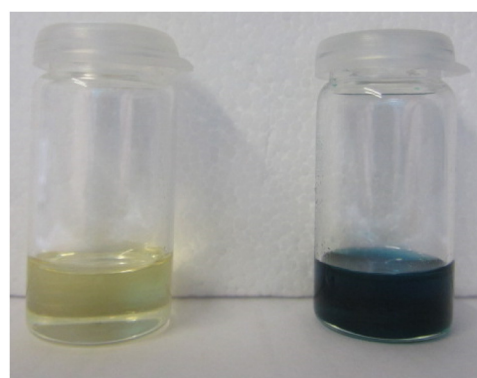
For copper, FIR measurements showed no  $\text{Cu-Cl}$  band in this range. Therefore we can conclude that copper is differently extracted than cadmium.

The results of the metal extractions indicated that the physicochemical properties of the ILs show only a minor impact on the extraction efficacy. This is in contrast to some reports in the literature [32], where ammonium- and phosphonium-based ILs possessed different extraction behavior. One explanation could be the high affinity of the thioglycolate anion towards cadmium and copper and hence its dominance in this case. Table 2 demonstrates distribution ratios for cadmium(II) and copper(II) after 120 min.

### 3.5. Back-extraction experiments

Based on the excellent extraction efficacies for Cd and Cu, the recycling and reusability properties were determined. The metal-containing IL was treated with an aqueous solution of stripping agent to remove the metal. The unloaded IL was then reused for further metal extraction. The back-extraction behavior was investigated using different agents, 0.5 M  $\text{HNO}_3$ , 1 M  $\text{HNO}_3$ , 0.5 M EDTA (pH 7) and 0.5 M HCl, respectively. These reagents showed good performance for  $[\text{BuGBOEt}][\text{Dca}]$  (tri(*n*-butyl)[2-ethoxy-2-oxoethylammonium dicyanamide) for copper removal [10] and cadmium has been successfully back-extracted from  $[\text{C}_4\text{MIM}][\text{PF}_6]$  using HCl, HF and  $\text{HNO}_3$  [45]. In the present case  $[\text{N}_{1888}][\text{C}_6\text{SAC}]$  was used for back-extraction experiments, as this IL showed the lowest leaching and the best extraction yields.

In Fig. 6, the extraction and back-extraction percentages using 0.5 M  $\text{HNO}_3$  for Cd(II) are shown for five cycles. After each cycle, the metal content in the aqueous phase was determined. Experimentally it was found that aqueous  $\text{HNO}_3$  can successfully strip  $\text{Cd}^{2+}$



**Fig. 7.** Snapshot before (left) and after (right) copper extraction from  $[\text{N}_{1888}][\text{BnSAC}]$ .

from  $[\text{N}_{1888}][\text{C}_6\text{SAC}]$ . In the first cycle, 72% of the loaded Cd was back-extracted after 1 h from the IL. Cd was recovered in excellent yields in the following cycles by aqueous nitric acid indicating no loss in performance of the IL. The IL is regenerated in the back-extraction process and these cycles indicate that  $[\text{N}_{1888}][\text{C}_6\text{SAC}]$  can be productively used for Cd extraction where its reusability guarantees a cost-efficient recycling of the IL.

For 0.5 M EDTA and 0.5 M HCl, no sufficient extraction and back-extraction efficacies were observed for both cadmium and copper, comparable with previously reported results [9,43].

The best back-extraction efficacy for copper was achieved by using 1 M  $\text{HNO}_3$  and sat.  $\text{KHCO}_3$  (Fig. S3 and S4). Studies with higher concentrations of nitric acid did not increase the back-extraction efficiency for Cu(II); however, a two-step separation approach produced an improvement in performance. This is in accordance to Yang and coworkers where selective recoveries for a broad range of lanthanides and transition metals using nitric and sulfuric acid were observed [46]. Firstly, the copper-loaded IL was treated with 1 M  $\text{HNO}_3$  followed by a neutralization step with sat.  $\text{KHCO}_3$ . This second step is essential due to the protonation of the respective thioglycolate under the applied harsh back-extraction conditions. Therefore washing of the depleted IL with  $\text{KHCO}_3$  deprotonates and activates the formed thioglycolic acid. These modifications allow successful removal of copper from the applied IL.

### 3.6. Immobilized ionic liquids on polypropylene hollow fibers

Since high viscosity can hinder the mass transfer during a bulk extraction process, solid polymeric carriers for the ILs were also investigated. Therefore the ILs were immobilized in polypropylene

**Table 3**

Leaching percentages (%) for immobilized ionic liquids from 100 mg IL into the aqueous phase.

	2 h	6 h
[N <sub>1888</sub> ][C <sub>4</sub> SAC]	0.1	0.3
[N <sub>1888</sub> ][C <sub>5</sub> SAC]	0.1	0.3
[N <sub>1888</sub> ][C <sub>6</sub> SAC]	0.1	0.2
[N <sub>1888</sub> ][BnSAC]	0.1	0.4
[P <sub>1888</sub> ][C <sub>4</sub> SAC]	0.1	0.4
[P <sub>1888</sub> ][C <sub>5</sub> SAC]	0.1	0.4
[P <sub>1888</sub> ][C <sub>6</sub> SAC]	0.1	0.2
[P <sub>1888</sub> ][BnSAC]	0.1	0.5

hollow fibers where the pores of the fibers can be brought into contact with the solution to be extracted. This established method is used for pre-concentration of silver from aqueous matrices [29]. As shown in Table S4, more than 90% of Cd(II) was extracted by all immobilized ILs after 6 h. In comparison to the free IL the extraction efficacy is slower for the immobilized ILs, where more than 95% of Cd(II) was extracted after 30 min. For copper, the extraction is not completed after 6 h and the [P<sub>1888</sub>]<sup>+</sup> derivatives showed better extraction efficacies than their [N<sub>1888</sub>]<sup>+</sup> counterparts (Table S5). In the case of [N<sub>1888</sub>][C<sub>4</sub>SAC] less than 50% was removed after 6 h. We can conclude that the solid-liquid extraction is slower with both metals than the bulk liquid extraction.

Leaching results, collected in Table 3, show a degree of extraction of the IL into the aqueous phase. The trend of decreasing leaching by higher lipophilicity is confirmed by our measurements. Among the immobilized ILs, [C<sub>6</sub>SAC]-based ILs showed the lowest dissolved carbon values, respectively (Table 3). We consider these immobilized ILs to be applicable to cadmium and copper extraction useful in a continuous process.

#### 4. Conclusions

This paper presents the synthesis and characterization of eight novel TSILs based on thioglycolic acid as well as methyltriocetylammmonium and methyltriocetylphosphonium. The desired products were obtained via an improved straight-forward two-step synthesis in very good yields (>80% overall) and high purity. The obtained ILs were characterized by standard analytical methods and their halide impurities have been quantified. Additionally, physicochemical properties and the thermal behavior of the ILs were determined. Walden plots of the ILs showed that most of the investigated compounds can be classified as good ILs with regard on ionicity. All ILs show deliquescence whereas neat ILs were found to be more viscous. We have clearly shown that the extraction process for cadmium is quick and efficient where more than 90% of cadmium was extracted after 30 min. Aqueous nitric acid was successfully used for repeatable back-extraction for cadmium and copper loaded [N<sub>1888</sub>][C<sub>6</sub>SAC]. From the outcome of our investigated extractions it is possible to conclude that the extraction of copper(II) is slower; nevertheless, more than 90% was removed by [P<sub>1888</sub>][C<sub>5</sub>SAC], [P<sub>1888</sub>][C<sub>6</sub>SAC] and [P<sub>1888</sub>][BnSAC] after 30 min. Overall, the developed alkyl thioglycolate ILs possess great potential for applications as heavy metal extractants.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2016.10.054>.

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