



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



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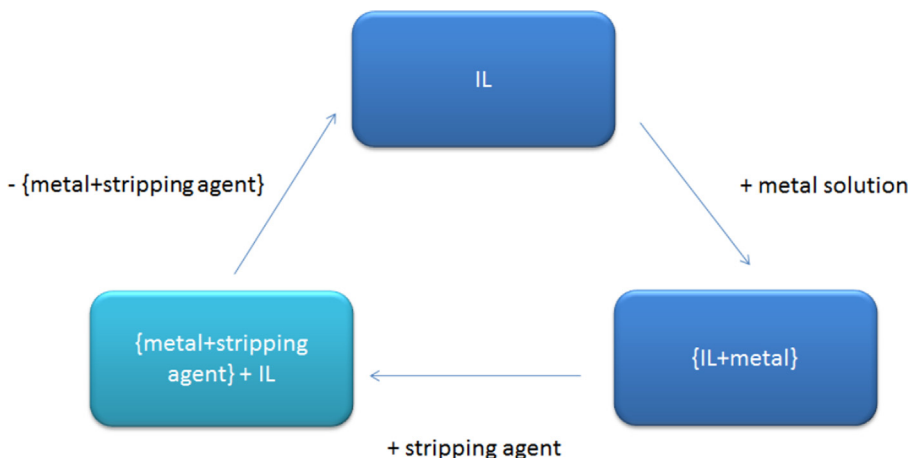
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### HIGHLIGHTS

- 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



### ARTICLE INFO

#### Article history:

Received 31 May 2016

Received in revised form

26 September 2016

Accepted 24 October 2016

Available online 24 October 2016

#### Keywords:

Thioglycolic acid

Task-specific ionic liquids

Heavy metal extraction

Immobilization

Reusability

### 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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## 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. Methyltrioctylphosphonium methylcarbonate (99%) ([TOMP][MC]) and methyltrioctylammonium 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  $\mu\text{m}$  internal diameter (75% porosity and 0.2  $\mu\text{m}$  pore size) obtained from Membrana (Germany).

### 2.2. Synthesis

Eight ionic liquids (Fig. 1), namely methyltrioctylammonium butylsulfanyl acetate [N<sub>1888</sub>][C<sub>4</sub>SAc], methyltrioctylammonium pentylsulfanyl acetate [N<sub>1888</sub>][C<sub>5</sub>SAc], methyltrioctylammonium hexylsulfanyl acetate [N<sub>1888</sub>][C<sub>6</sub>SAc], methyltrioctylammonium benzylsulfanyl acetate [N<sub>1888</sub>][BnSAc], methyltrioctylphosphonium butylsulfanyl acetate [P<sub>1888</sub>][C<sub>4</sub>SAc], methyltrioctylphosphonium pentylsulfanyl acetate [P<sub>1888</sub>][C<sub>5</sub>SAc], methyltrioctylphosphonium hexylsulfanyl acetate [P<sub>1888</sub>][C<sub>6</sub>SAc] and methyltrioctylphosphonium 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

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