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Greener synthesis of new ammonium ionic liquids and their potential as extracting agents

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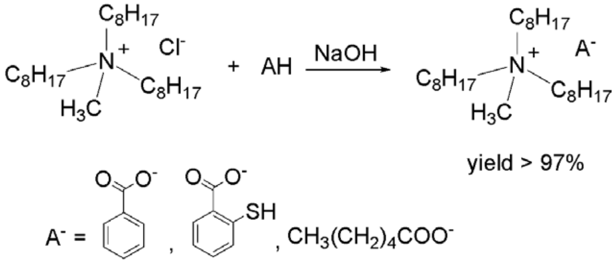
Abstract

New hydrophobic ionic liquids were synthesized from tricaprylmethylammonium chloride (Aliquat 336©) and selected Bronsted acids by a sustainable, simple and cost-saving deprotonation-metathesis route. Prepared ionic liquids were evaluated as potential extracting agents for cadmium from different aqueous solutions. High efficiency and selectivity were reached for the extraction of cadmium from a natural river matrix with tricaprylmethylammonium thiosalicylate, [A336][TS], a thiol-containing task specific ionic liquid.

The synthesis of ionic liquids (ILs), their characterization, and possible applications have been developing progressively, as the properties of this class of organic salts with melting points below the boiling point of water have gained intensive attention in nearly all fields of chemistry. Furthermore, through the incorporation of functional groups, the synthesis of task specific ILs (TSILs) has been a focus of research, leading to tailor-made substances for desired applications.[1]

A widespread research field is the use of ILs as well as TSILs incorporating disulfide-, thioether-, urea- or hydroxybenzylamine groups as extracting agents for metals.[2–7] Most of ILs or TSILs for extracting applications described in the literature are based on imidazolium-, piperidinium-, pyrrolidinium- and pyridinium cations and fluorine containing anions, whereas diverse functional groups are generally appended to the cation.[3–7] In contrast, the newly synthesized ILs described here are based on a hydrophobic, long chain tetraalkylammonium cation with aliphatic and aromatic carboxylate anions. Furthermore, tricaprylmethylammonium thiosalicylate, [A336][TS], possesses a thiol-containing anion.

New ammonium ILs were prepared by stirring equimolar amounts of Aliquat 336© as a precursor and selected Bronsted acids in a sodium hydroxide solution. Deprotonation of the acid followed by anion metathesis led to the desired ionic liquids (Scheme 1). Aliquat 336© is actually an ionic liquid itself and is regarded as a 2:1 mixture of methyl trioctylammonium- and methyl tridecylammonium chloride with a proposed mean molar weight of 432 g/mol.[8] We investigated the structure of the Aliquat 336©-cation and positive ion mode electrospray ionization-mass spectrometry (ESI-MS) disclosed peaks that could be assigned to methyl tricapryl cations containing either octyl- or decylchains or mixtures of them. However, one peak could clearly be assigned to an existing methyl



Scheme 1. Synthesis of tricaprylmethylammonium based ionic liquids.

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dioctylhexylammonium cation. Interestingly, including a methyl dioctylhexylammonium cation in molar weight calculations, a mean value of 432 g/mol is also obtained for Aliquat 336© and was therefore used throughout our synthesis.

The deprotonation-metathesis route is simple, fast and sustainable since water is the only solvent used and sodium chloride the sole by-product. Tricaprylmethylammonium thiosalicylate, [A336][TS], tricaprylmethylammonium benzoate, [A336][BA] and tricaprylmethylammonium hexanoate, [A336][Hex] were obtained in yields around 97% and characterization data showed that ILs exhibit a good quality.

In Figure 1a the ^{1}H-proton spectrum of [A336][TS] is shown. Chemical shifts between 6.68 and 7.87 ppm could clearly be assigned to aromatic hydrogen atoms of the thiosalicylate anion. FTIR spectra of precursors Aliquat 336© and thiosalicylic acid as well as the resulting IL [A336][TS] are shown in Figure 1b. Typical absorption bands of the carboxylic acid diminished after the reaction, indicating that the deprotonation was successful. New absorption bands at 743, 1466 and 1562 cm^{-1} could be assigned to stretching and bending vibrations of aromatic C–H groups. Interestingly, an expected absorption band of the thiol group near 2500 cm^{-1} could not be observed for the prepared [A336][TS]. This may be attributable to the generally

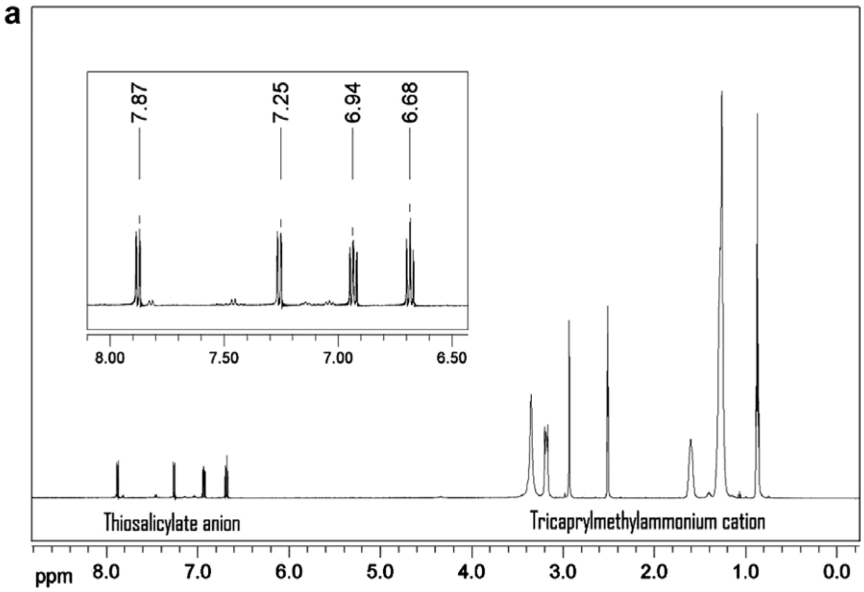

Fig. 1a. ^{1}H NMR spectrum of [A336][TS].

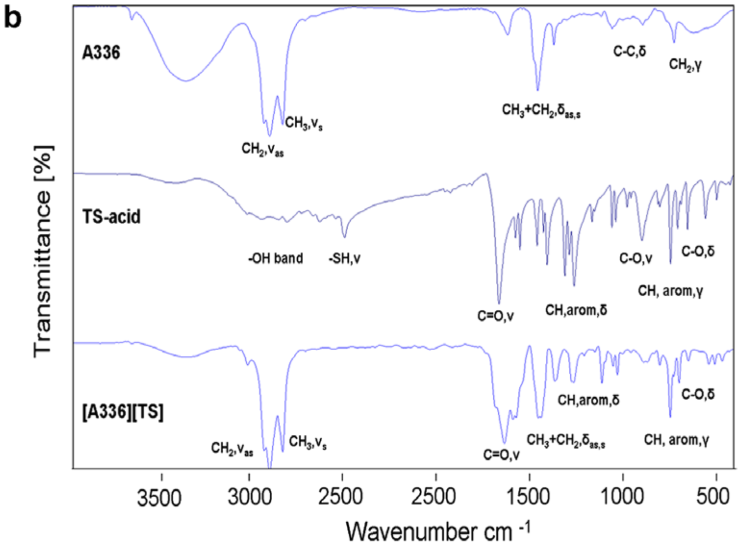

Fig. 1b. FTIR spectra of Aliquat 336© (A336), thiosalicylic acid (TS-acid) and ionic liquid [A336][TS].

Table 1
Physicochemical properties of Aliquat 336©-based ionic liquids

Ionic liquid	Physical state (25 °C)	Decomp. T/°C	Cl$^-$ cont. (wt %)	ρ/g cm^{-3} (20 °C)	Solubility[a]	
					Miscible	Immiscible
[A336][TS]	Liquid	202	<0.1	0.96	ea, ac, m, e, an	w
[A336][BA]	Liquid	161	0.81	0.96	ea, ac, m, e, an	w
[A336][Hex]	Liquid	148	0.59	0.89	ea, ac, m, e, an	w

[a] Observed solubility of ionic liquids: complete solubilization (miscible) or non-solubilization (immiscible), where w = water, ea = ethylacetate, ac = acetone, m = methanol, e = ethanol, an = acetonitrile.

considered low intensity of this band. ESI-MS experiments proved that the thiol group was not deprotonated: in case of an additional deprotonation of the thiol group, a peak at a lower mass to charge ratio should have been observable. A single peak at $m/z = 153.2$ could clearly be assigned to the thiosalicylate anion. Generally, negative ion mode ESI-MS spectra of all prepared ILs showed signals corresponding to the according aliphatic or aromatic anion.

Measured physicochemical properties of synthesized ILs are given in Table 1. [A336][TS], [A336][BA] and [A336][Hex] were liquid at room temperature and immiscible with water but miscible with common organic solvents such as ethyl acetate, acetone, ethanol, methanol and acetonitrile. Thermogravimetric analysis showed decomposition temperatures of prepared ILs between 148 °C and 202 °C. Measured chloride contents were between <0.10 and 0.81 wt %.[9] These values are lower compared to most of the reported values for ammonium ionic liquids prepared from Aliquat 336© applying other synthesis routes.[2] Obtained densities of ILs with aromatic anions [TS] and [BA] were higher compared to the aliphatic IL [A336][Hex]. These results are in accordance with the assumption of Kulkarni et al.[10] proposing an increase in the bulkiness of the anion leading to an increase in density.

As prepared ILs contain a carboxylic functionality and [A336][TS] additionally a thiol group, they were evaluated as potential extracting agents for cadmium from different aqueous solutions. Ultrapure water as well as a filtrated (0.45 µm) natural fluvial water matrix was spiked with a cadmium standard solution obtaining a total concentration of 4 ppm/L. To evaluate the extraction potential of ILs under neutral conditions and the influence of a natural buffered fluvial system, the pH-value of the water samples was kept at the pH as measured after spiking with metal standard.[†]

The extraction efficiency of ILs for cadmium from ultrapure water and natural river water (Fig. 2) follows the order [A336][TS] $\gg$ [A336][Hex] > [A336][BA].

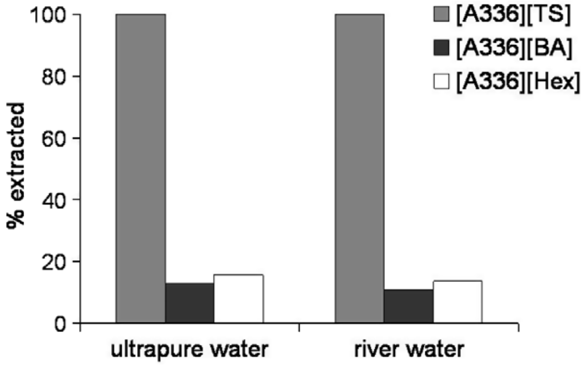

Fig. 2. Extraction efficiency of evaluated ionic liquids for the extraction of cadmium from ultrapure water and a natural river sample.

In ultrapure water, extraction efficiencies of >99.9% were obtained for [A336][TS], 16% for [A336][Hex] and 13% for [A336][BA]. For the elimination of cadmium from river water [A336][TS] showed an efficiency of >99.9%, [A336][Hex] 14% and [A336][BA] 11%.

As the difference in structure between [A336][TS] and [A336][BA] is a thiol group appended to the anion of [A336][TS], it seems obvious that this group has an important influence on the extraction process. There were no remarkable differences in extraction efficiencies between evaluated aliphatic and aromatic carboxylic ILs [A336][Hex] and [A336][BA].

Interestingly, a natural river matrix did not lead to a decrease of extraction efficiency for evaluated ILs. Calculated distribution coefficients for alkali- and earth alkali metals with [A336][TS] are given in Table 2 and are below a value of 2, whereas a distribution coefficient of >10,000 could be stated for cadmium. [A336][TS] is therefore very efficient and selective for the extraction of cadmium from a river matrix with natural occurring alkali- and earth alkali cations. This may be interesting for extraction tasks

Table 2
Distribution coefficients (D) for [A336][TS] for the extraction of metals from a natural river matrix

Cation	D ([A336][TS])
Na^+	0.14
K^+	0.14
Ca^{2+}	1.49
Mg^{2+}	0.10
Cd^{2+}	>10,000

[†] 0.5 ml of IL and 8 ml of cadmium containing water phase were shaken for 10 min, followed by centrifugation at 3500 rpm. The water phase was separated from the IL phase and acidified for measurements. Flame atomic absorption spectroscopy (F-AAS) was used for quantization of cadmium concentrations in the water phase before and after the extraction process. Additionally, alkali and earth alkali elements of natural river water were measured to evaluate the selectivity of ILs for the extraction of cadmium compared to naturally occurring metals. Extraction efficiency of >99.9% was assumed when measured values were below detection limit of the corresponding method.

where hard water with high calcium and magnesium concentrations is present.

Compared to other cadmium extracting agents, working well under neutral conditions, on which research was recently published,[11–15] [A336][TS] displays some considerable advantages: the selectivity for cadmium is well comparable to calix[4]arene derivates bearing pyridinium or sulfur-containing units in the presence of alkali metal ions.[11–13] The extracting efficiency of [A336][TS] (>99.9%) lies even above these compounds and its use may be regarded to as more sustainable, as no volatile and flammable organic solvents are needed. Other environmental friendly, low-cost biomaterials, for example, biofilm covered granular activated carbon,[15] or crab shells,[14] showing adsorption of organic residues or slow sorption kinetics, respectively, are outnumbered by [A336][TS] displaying an undisturbed fast metal uptake and a high affinity for cadmium under neutral conditions, even in a complex natural matrix.

Current investigations deal with the affinity of [A336][TS] for other metals. In addition, the elucidation of the reaction mechanism as well as the design of a suitable recycling process for a reuse of the applied ILs by metal stripping is of considerable interest.

In conclusion, we demonstrated the successful preparation of three new hydrophobic ammonium ionic liquids from Aliquat 336© as a cation source and Bronsted acids as anion sources. Moreover, preliminary investigations have shown that the implementation of functional groups (e.g., thiol) onto the anion is leading to task specificity in ionic liquids usable as extracting agents.

Due to our results, we are convinced that the presented deprotonation-metathesis route may be an elegant way for the preparation of further numerous hydrophobic Aliquat 336 ©-based ILs with functionalities appended to the anion.

Acknowledgements

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Supplementary data

Supplementary data (Section I: preparation and characterization of ionic liquids including general synthesis route and applied characterization methods. Additionally ^{1}H and ^{13}C NMR shifts, FTIR and ESI/MS spectra and density versus temperature charts of the three synthesized ionic liquids and Aliquat336® as precursor are presented. Section II: experimental part including applied analytical methods (Flame-AAS and IC)) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.02.138.

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