Radionuclide extraction with different ionic liquids

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Abstract

10 ionic liquids based on 3 different cations and 5 anions were investigated for radionuclide extraction from aqueous solutions. While uranium and ²¹⁰Po were extracted with satisfying yields irrespective of the feed solution pH, ²³⁴Th, ²²⁶Ra and ²¹⁰Pb extraction yields were rather low. The contact time necessary for near to complete extraction was determined as well as the conditions for successful back-extraction. The loading capacities of the ionic liquids for uranium were very high and depended on the uranyl counter-ion. From the leaching of the ionic liquids into the aqueous phase the predominant extraction mechanisms were derived.

Keywords Ionic liquids · Radionuclide extraction · Maximum uranium uptake · Leaching to the aqueous phase

Introduction

Generally, the term ionic liquid (IL) refers to salts with melting points below 100 °C. Some of them are liquid even at room temperature. The low melting points typically result from the combination of a bulky asymmetric organic cation, as e.g. imidazolium, pyridinium, pyrrolidinium, ammonium and phosphonium, with a smaller anion. They usually exhibit a very low (often negligible) vapor pressure, high decomposition temperatures and high electrical stability [1, 2]. Moreover, their physico-chemical properties can often be fine-tuned by modifying either the cation or the anion.

At our institute ILs which can be produced in a straightforward metathesis reaction from cheap precursor molecules were tested for their ability to extract heavy metals such as Ag, Cd, Co, Cu, Hg, Mn, Ni, Pb, Pt and Zn from different water samples as e.g. surface waters or waste waters [3–8]. As radionuclides in drinking water is an important issue in radiation protection it was obvious to test some of these ILs (primarily those which had already been used successfully for inactive metal extraction) also for extraction of uranium and thorium [9] and later on also for ²²⁶Ra, ²¹⁰Pb, ²¹⁰Bi and ²¹⁰Po [10]. Methyltrioctylammonium thiosalicylate [N1888] [TS] had shown very good uranium extraction efficiencies,

and also methyltrioctylammonium maltolate [N1888] [Mal] and tetradecyltriethylphosphonium maltolate [PR4] [Mal] (also known as [C101] [Mal]) extracted uranium and ²¹⁰Po within short times, while the other radionuclides were removed from water to a much lesser extent and often with strong dependence of the pH value.

In the last years new ILs were synthesized and successively investigated for radionuclide extraction from water samples. Only 3 different cations (methyltrioctylammonium [N1888], methyltrioctylphosphonium [P1888] and tetradecyltriethylphosphonium [PR4]) were combined with 5 anions (anthranilate [Ant], 2-hydroxy-5-nitrobenzoate [HNBA], 2-(hexylthio)acetate [C6SAc], 4-aminosalicylate [ASA], and thiosalicylate [TS]) and in sum 10 ILs were tested (see Table 1). Additionally to the extraction efficiencies we investigated the time necessary for satisfying (i.e. near to complete) extraction and the maximum uranium load that can be taken up by the respective IL. Another important task was to quantify the leaching of the ILs to the aqueous phase, which can often also give some hints regarding the extraction mechanism. This paper gives a compilation of these results.

Materials and methods

The investigated ILs were [N1888] [Ant], [N1888] [HNBA], [N1888] [C6SAc], [N1888] [ASA], [P1888] [TS], [P1888] [Ant], [P1888] [C6SAc], [PR4] [Ant], [PR4] [HNBA], and

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Table 1 Cations and anions of the investigated ILs

Methyltrioctylammonium [N1888]
Methyltrioctylphosphonium [P1888]
Tetradecyltriethylphosphonium [PR4]
Anthranilate [Ant]
2-hydroxy-5-nitrobenzoate [HNBA]
4-aminosalicylate [ASA]
Thiosalicylate [TS]
2-(hexylthio)acetate [C6SAc]

[PR4][ASA]. All of them were highly viscous substances comparable to oils or honey, with colors from white to yellow, orange, brown and dark brown. Their densities were all below 1 g cm⁻³. The ILs had been synthesized from the relatively cheap and commercially available precursor ILs methyltrioctylphosphonium methylcarbonate [TOMP][MC] (available from Henkel), methyltrioctylammonium methylcarbonate [TOMA][MC] (again available from Henkel), and Cyphos[®]IL 101 (available from Cytec) by colleagues from our institute. [TOMP] and [TOMA] are synonyms for [P1888] and [N1888], respectively, and Cyphos[®]IL 101 is a synonyme for [PR4][Cl]. The purity of the synthesized ILs

had been checked by NMR, ESI-MS and IR measurements and was indicated as highly satisfying [4, 5].

For the extraction experiments in-house standard solutions of uranyl nitrate and uranyl acetate (containing also ²³⁴Th in radioactive equilibrium with uranium), ²²⁶Ra (as chloride, with known amounts of ingrown ²¹⁰Pb and ²¹⁰Po) as well as ²¹⁰Pb (as chloride, containing also equilibrium concentrations of ²¹⁰Po) were used. The respective α -activity concentrations of uranium (together with its β -emitting progeny ²³⁴Th) were measured in aliquots of the aqueous phase before and after extraction by liquid scintillation counting (LSC) using the water-miscible cocktail Optiphase HiSafe[™] III (Perkin Elmer) and a Quantulus[™]1220 low-level liquid scintillation counter (Wallac Oy, Finland, now Perkin Elmer) [9, 10]. For simultaneous measurement of the α - and β -spectra pulse-shape analysis was used. The same technique was used for a ²¹⁰Pb (β -emitter) solution, containing also ²¹⁰Po (α -emitter) in radioactive equilibrium. ²²⁶Ra was measured via ²²²Rn and progenies collected in a water-immiscible mineral-oil cocktail (NEF-957 A, Packard Bioscience) after a waiting period of about 2 weeks [11]. After ²²²Rn determination the aqueous phase was separated from the mineral-oil cocktail and ²¹⁰Po was measured after spike-addition (²⁰⁹Po) and electrodeposition on a Cu-planchet by alpha-spectrometry using a PIPS detector (Canberra) [12]. If a ²¹⁰Pb solution was used, the ²¹⁰Pb as well as the ²¹⁰Po were measured simultaneously by LSC of an aliquot of the aqueous phase mixed with the water-miscible cocktail Optiphase HiSafe[™] III (Perkin Elmer) using pulse-shape analysis. Generally, all measurements were done on triplets (see below).

Extraction efficiency and feed solution pH

The respective radionuclide solution was added to 40 mL of distilled water, giving a concentration of 11.6 mg L⁻¹ uranium (0.048 mM, corresponding to an activity of 2.8 Bq per 10 mL sub-sample), 15 Bq L⁻¹ ²²⁶Ra and 11.7 Bq L⁻¹ ²¹⁰Pb. The required pH value was adjusted by adding diluted HNO₃ or NaOH. The pH was measured with an SI Analytics Lab 850 benchtop pH meter. From this solution 4 sub-samples (10 mL each) were taken. To 3 sub-samples 20 mg of IL was added and then this mixture was shaken overnight at 100 rpm. The 4th sub-sample was shaken without IL and provided a reference (giving the activity concentration in the samples before extraction). The samples were centrifuged for 30 min at RCF = 1640 to separate the IL from the aqueous phase. An aliquot of the aqueous phase (3 mL) was pressed through a syringe filter (cellulose acetate, pore size 0.2 μ m) to remove left-overs of the IL, mixed with scintillation cocktail and measured by LSC. The measured counts per minute (cpm) of the sample divided by the cpm of the reference sample gave the percentage of the non-extracted radionuclide.

Loading capacity/adsorption isotherms

The amount Q_e of uranium extracted into the IL (given in mg U/g IL) was calculated according to the equation

$$Q_e = \frac{(c_o - c_e)}{m} \times V$$

C_0 uranium concentration in the liquid phase before extraction (mg L^{-1}), C_e equilibrium uranium concentration in the liquid phase after extraction (mg L^{-1}), m mass of IL (g), V volume of aqueous phase (L).

From the Q_e values and the respective molecular masses we then calculated the mol U taken up per mol IL (mol%), which seemed for us a much more descriptive way of demonstrating high uptake.

Extraction experiments with initial uranyl nitrate concentrations ≤ 1 mM displayed near to complete uranium extraction after 24 h for all investigated ILs (see below). Already in our previous work [4, 5, 9] and also in the literature [13–16] high uranium loading capacities had been reported. To determine the maximum uranium load that can be taken up by different ILs, uranyl solutions with concentrations up to 6 mM had to be used. This investigation was done with uranyl nitrate as well as with uranyl acetate solutions to check for the influence of different aqueous counterions, in this case without pH adjustment to avoid additional ions. The pH values of all aqueous uranyl solutions investigated for loading capacities were between 3 and 4, so a significant influence from pH differences on the extraction efficiency seems unlikely.

Time-dependence of extraction efficiency

The so far described investigations of the aqueous sample pH influence as well as of the maximum uranium uptake used overnight shaking of the sample-IL-mixture. However, ILs used in extraction experiments with lower uranyl concentrations might require much shorter times for uranyl uptake with satisfying efficiency (near to complete extraction). So extraction efficiencies of 7 ILs were measured after different contact times with the aqueous solution (0.048 mM uranyl nitrate or acetate concentrations, without pH-adjustment).

Back-extraction

To be able to re-use the respective IL we tried to strip uranium and ^{234}Th (and in some experiments also the other radionuclides) from the metal-loaded IL phase by back-extraction.

As stripping agents 0.05 M EDTA, 0.05 M HCl and 0.05 M HNO_3 were used, which had already shown good stripping performance for non-radioactive metals [4, 5]. Our acid concentrations were lower by a factor of 10 compared to the above cited literature in order to avoid degradation of the IL. The shaking of the IL together with the stripping agent was again done overnight.

Leaching

In practice, successful use of ILs for metal or radionuclide extraction from water demands for stability upon contact with the aqueous phase, i.e. a negligible or only a very low amount of the IL should be dissolved in the aqueous phase after extraction, in order to minimize loss of the IL as well as to avoid water pollution. Aqueous solubility or leaching into the water phase is also known as “bleeding”, and different causes might be responsible for this process: solubility of the IL in the aqueous phase (which could be circumvented by using ions with higher hydrophobicity or by immobilization of the IL on an inert carrier [4, 5] or in an hollow fiber [6, 8]), or ion exchange as extraction mechanism. In the latter case the anion or cation of the IL is substituted by the metal or a metal compound and the leaching is part of the metal extraction mechanism.

Total organic carbon TOC and total nitrogen TN data (if nitrogen is present in the IL) provide information about IL leaching and can furthermore give some hints about the extraction process. The ILs [P1888][TS] and [P1888][Ant] were investigated with regard to these questions: TOC/TN values were measured after shaking 5 mL distilled water with 20 mg IL for 24 h (aqueous solubility), the same measurements were performed before and after shaking with 2 mM $\text{UO}_2(\text{NO}_3)_2$ and 2 mM $\text{UO}_2(\text{CH}_3\text{COO})_2$ solutions to investigate the influence of the various ions.

For the TOC/TN measurements, 1 mL of the sample solution was mixed with 11 mL of ultrapure water. A Shimadzu[®] TOC-V CPH total organic carbon analyzer with a Shimadzu[®] TNM-1 nitrogen measuring unit was used for quantifying TOC and TN contents. Samples were acidified with HCl and purged with synthetic air to remove inorganic carbon as CO_2 prior to the analysis. After sample injection into the combustion tube containing an oxidation catalyst at 720 °C, the nitrogen compounds were decomposed to nitrogen monoxide and carbon is oxidized. CO_2 was then detected by a nondispersive infrared sensor, which was connected in series to a chemiluminescence detector, where the gas-phase chemiluminescence of the various ozone plus nitrogen monoxide reaction products were detected at 50 °C. Additionally to the TOC/TN measurements, before and after extraction also the pH was measured.

Results and discussion

Extraction efficiency and feed solution pH

The results of the pH-dependence of the extraction capability are summarized in Table 2. All the investigated ILs extracted uranium and ^{210}Po with satisfying high efficiencies ($\geq 90\%$) irrespective of the pH-value. ^{234}Th extraction was strongly pH dependent and mostly below 90%. As Th isotopes usually do not occur in natural waters, Th is not an important issue in radiation protection. Nonetheless, in this work ^{234}Th at least in some cases was evaluated. ^{210}Pb was extracted with only low efficiencies ($\leq 40\%$). ^{226}Ra was not at all extracted by the ILs [N1888][Ant], [N1888][HNBA] and [P1888][C6SAC]. These results are comparable to the results of Platzer et al. [10] for [A336][Mal] and [C101][Mal] (please note that [A336] and [C101] is identical to [N1888] and [PR4], respectively).

The extraction efficiency measurements were performed until pH = 8 was reached as for higher pH values with uranyl samples a precipitate was observed after the centrifugation step.

Loading capacity/adsorption isotherms

Figure 1 shows the uranium uptake (given in μg uranium/mg IL) from uranyl nitrate and uranyl acetate solutions into the IL [PR4][HNBA]. Table 3 summarizes our results, giving the uranium uptake in mol% (i.e. mol U/mol IL). All investigated ILs showed higher uranyl extraction when the counterion was acetate compared to the counter ion nitrate. The IL anion [Ant] was able to take up 80–88 mol% uranyl from an acetate solution compared to only 25–38 mol% from a nitrate solution. The same tendency was observed also for the anions [C6SAC] (65 vs. 33 mol%), [HNBA] (88 vs. 56 mol%), and [TS] (51 vs. 25 mol%). For the ILs [N1888][Ant], [P1888][C6SAC] and [PR4][HNBA] the maximum

Table 2 Extraction efficiency (mean $\pm$ SD, $n = 3$) and feed solution pH

pH	[N1888][Ant]				pH	[N1888][HNBA]			
	U	Th	Po	Pb		U	Th	Po	Pb
2	74 $\pm$ 5	87 $\pm$ 5	90 $\pm$ 4	10 $\pm$ 2	2	99 $\pm$ 2	12 $\pm$ 3	98 $\pm$ 2	23 $\pm$ 5
4	94 $\pm$ 3	82 $\pm$ 5	96 $\pm$ 3	76 $\pm$ 2	4	99 $\pm$ 2	26 $\pm$ 3	98 $\pm$ 2	30 $\pm$ 4
6	95 $\pm$ 3	72 $\pm$ 4	97 $\pm$ 3	46 $\pm$ 5	6	99 $\pm$ 2	21 $\pm$ 2	99 $\pm$ 2	30 $\pm$ 4
7	96 $\pm$ 2	86 $\pm$ 4	91 $\pm$ 4	31 $\pm$ 4	7	99 $\pm$ 2	36 $\pm$ 3	99 $\pm$ 2	25 $\pm$ 5
8	99 $\pm$ 2	83 $\pm$ 5	92 $\pm$ 4	32 $\pm$ 4	8	99 $\pm$ 2	25 $\pm$ 3	97 $\pm$ 2	25 $\pm$ 5
pH	[N1888][C6SAC]				pH	[N1888][ASA]			
	U	Th	Po	Pb		U	Th	Po	Pb
2	45 $\pm$ 4	56 $\pm$ 4	96 $\pm$ 2	–	2	90 $\pm$ 4	14 $\pm$ 8	60 $\pm$ 10	0
4	99 $\pm$ 2	41 $\pm$ 3	93 $\pm$ 2	–	4	97 $\pm$ 2	60 $\pm$ 10	72 $\pm$ 6	0
6	99 $\pm$ 2	99 $\pm$ 2	97 $\pm$ 1	–	6	98 $\pm$ 2	50 $\pm$ 10	75 $\pm$ 5	9 $\pm$ 5
7	98 $\pm$ 2	76 $\pm$ 4	–	–	7	–	–	–	–
8	92 $\pm$ 2	29 $\pm$ 4	–	–	8	99 $\pm$ 1	88 $\pm$ 4	88 $\pm$ 4	35 $\pm$ 10
pH	[P1888][C6SAC]				pH	[PR4][HNBA]			
	U	Th	Po	Ra		U	Th	Po	Pb
2	45 $\pm$ 5	–	96 $\pm$ 4	3 $\pm$ 1	2	99 $\pm$ 2	95 $\pm$ 5	99 $\pm$ 2	26 $\pm$ 6
4	97 $\pm$ 3	–	93 $\pm$ 5	4 $\pm$ 1	4	99 $\pm$ 2	99 $\pm$ 3	97 $\pm$ 3	6 $\pm$ 6
6	98 $\pm$ 2	–	97 $\pm$ 3	0	6	99 $\pm$ 2	84 $\pm$ 6	97 $\pm$ 3	14 $\pm$ 10
8	90 $\pm$ 4	–	97 $\pm$ 3	0	8	99 $\pm$ 2	69 $\pm$ 7	98 $\pm$ 2	0
pH	[PR4][ASA]				pH	[PR4][Ant]			
	U	Th	Po	Pb		U	Th	Po	Pb
2	70 $\pm$ 10	–	86 $\pm$ 5	0	2	98 $\pm$ 2	36 $\pm$ 3	91 $\pm$ 5	14 $\pm$ 10
4	98 $\pm$ 2	–	88 $\pm$ 4	45 $\pm$ 15	4	99 $\pm$ 1	59 $\pm$ 3	93 $\pm$ 4	42 $\pm$ 5
6	98 $\pm$ 2	–	90 $\pm$ 3	77 $\pm$ 8	6	99 $\pm$ 1	47 $\pm$ 3	86 $\pm$ 5	36 $\pm$ 8
8	99 $\pm$ 2	–	91 $\pm$ 3	24 $\pm$ 15	8	92 $\pm$ 3	59 $\pm$ 3	89 $\pm$ 3	36 $\pm$ 8

– Not measured

Fig. 1 Uranium uptake in [PR4][HNBA]. Relative uncertainties of Q_{eq} values are $\leq 5\%$

loading capacity for the uranyl ion from an acetate solution was not even reached, as can be seen in Fig. 1. The respective values in Table 2 are therefore minimum values.

It should be mentioned that some ILs displayed signs of degradation in extraction experiments utilizing high uranyl concentrations in the scale of the loading capacity: [P1888][Ant] showed crystallization of a light yellow solid on the edges of the IL phase, visibly disintegrating

at high initial uranyl concentrations. With [P1888][TS] a white precipitate appeared in extractions using large amounts of uranyl nitrate, while high concentrations of uranyl acetate solutions evoked leaching of [P1888][TS] to the aqueous phase. This sets a limit to high loading in practical applications.

Time-dependence of extraction efficiency

While [P1888][C6SAC] and [N1888][Ant] showed complete uptake for the uranyl from nitrate as well as acetate solutions already after 10 min, [N1888][C6SAC], [N1888][HNBA], [PR4][HNBA], [P1888][Ant] and [P1888][TS] took longer for complete uptake. Figure 2 summarizes our results. After 1 h contact time [N1888][C6SAC] reached full extraction from both uranyl solutions as well as [PR4][HNBA] from acetate solutions (from nitrate solutions for this IL 2 h were necessary). For [P1888][Ant] complete extraction needed 2.5 h from both uranyl solutions, while [P1888][TS] and [N1888][HNBA] needed even longer (here the minimum times for complete extraction were not determined, but after overnight shaking the extractions were near to 100%).

Table 3 Uranium uptake from uranyl nitrate and uranyl acetate solutions of different ILs

IL	Uptake from uranyl nitrate (mol%)	Uptake from uranyl acetate (mol%)	IL	Uptake from uranyl nitrate (mol%)	Uptake from uranyl acetate (mol%)
[N1888][Ant]	38 ± 2	83 ± 4	[N1888][C6SAC]	30 ± 2	62 ± 3
[P1888][Ant]	33 ± 2	88 ± 5	[P1888][C6SAC]	33 ± 2	65 ± 4
[PR4][Ant]	25 ± 1	80 ± 4	[PR4][HNBA]	56 ± 3	88 ± 5
			[P1888][TS]	25 ± 1	51 ± 3

Fig. 2 Extraction versus contact time for different ILs

Back-extraction

The experiments with 0.05 M EDTA to strip uranium from the ILs did not give satisfying yields, contrary to the diluted acids. Both acids gave similar results in the first experiments; we decided on HNO_3 for further investigations.

Our results are summarized in Table 4. Uranium, ^{234}Th , ^{210}Pb and ^{210}Po back-extraction with 0.05 M HNO_3 as stripping agent was investigated for the ILs [N1888][Ant], [N1888][HNBA], [PR4][Ant] and [PR4][HNBA]. The last one showed the poorest stripping results: none of the investigated radionuclides could be stripped from the IL phase. Generally, ^{210}Po could not be stripped from any of the investigated ILs. For [N1888][HNBA] only the ^{210}Pb back-extraction worked with a reasonable yield of 70%. The same and even higher yields (95%) for ^{210}Pb gave [N1888][Ant] and [PR4][Ant], respectively. For these ILs, however, the previous ^{210}Pb extraction yields had been rather low. Uranium was stripped with only 39% yield from [PR4][Ant] and with 82% yield from [N1888][Ant]. Higher uranium stripping yields were found for the ILs [PR4][ASA] and [N1888][C6SAc], respectively, but these ILs were not investigated with regard to the other radionuclides.

It has to be emphasized that recovering the extracted metals is also possible by destroying the IL phase with concentrated acids. So a concentration of the radionuclides in a smaller aqueous volume is always possible, but of course the IL in that case cannot be re-used.

Leaching

Table 5 shows the results of the leaching experiments with [P1888][Ant] and [P1888][TS]. 24 h contact with distilled water resulted in significantly stronger leaching for [P1888][Ant] (174.8 mg/L TOC compared to only 14.8 mg/L for [P1888][TS]), which can be explained by the higher hydrophobicity of the thiol group compared to the amine. Compared to other [P1888] or [N1888] containing ILs, the aqueous solubility for [P1888][TS] is in the lower range [3, 5, 10]: only 0.5% of the IL has leached into the aqueous phase after 24 h. For [P1888][Ant] this value was clearly higher (6%). Here, the presence of nitrogen in the anion allowed calculating the concentrations of both ions in the aqueous phase, which showed that leaching to pure water was asymmetric, as for the ion concentrations holds $[\text{Ant}] = 1.6 \cdot [\text{P1888}]$. Probably protonation of [Ant] to

Table 4 Radionuclide back-extraction yield of various ILs

	[N1888][Ant]	[N1888][HNBA]	[N1888][C6SAc]	[PR4][Ant]	[PR4][HNBA]	[PR4][ASA]
U	82%	16%	96%	39%	5%	89%
Th	93%	0	—	52%	0	—
Po	2%	0	—	3%	0	—
Pb	70%	70%	—	95%	0	—

Relative uncertainties of results are around 10%

Table 5 Leaching of two ILs to distilled water, uranyl nitrate and uranyl acetate solutions

	TOC (mg/L)	TN (mg/L)	N (μmol)	U (μmol)	pH
<i>[P1888][Ant]</i>					
Dist. water	174 $\pm$ 20	8.8 $\pm$ 0.3	3.2 $\pm$ 0.1	—	
$\text{UO}_2(\text{NO}_3)_2$					
Before	—	90.0	32.2	10.2 $\pm$ 0.1	2.6
After	135 $\pm$ 22	28.2 $\pm$ 0.7	10.1 $\pm$ 0.3	0.018 $\pm$ 0.0004	3.0
$\text{UO}_2(\text{CH}_3\text{CO}_2)_2$					
Before	150	—	—	11.4 $\pm$ 0.2	4.4
After	1223 $\pm$ 75	6.2 $\pm$ 1.2	2.2 $\pm$ 0.4	0.2 $\pm$ 0.1	4.9
<i>[P1888][TS]</i>					
Dist. water	14.8 $\pm$ 0.8	—	—		
$\text{UO}_2(\text{NO}_3)_2$					
Before	—	89.4	31.9	10.1 $\pm$ 0.1	2.6
After	12.2 $\pm$ 0.6	52.1 $\pm$ 0.5	18.6 $\pm$ 0.2	2.6 $\pm$ 0.09	2.5
$\text{UO}_2(\text{CH}_3\text{CO}_2)_2$					
Before	144	—	—	11.2 $\pm$ 0.1	4.4
After	228 $\pm$ 27	—	—	0.26 $\pm$ 0.03	3.8

Table 6 TOC, TN and pH data for shaking experiments with 20 mg IL and different aqueous solutions after 24 h at 300 rpm

	TOC (mg/L)		TN (mg/L)		pH	
	Before	After	Before	After	Before	After
[P1888][Ant]						
Pure water	–	174 ± 20	–	8.8 ± 0.3	6.3	5.9
HNO ₃ 5 mM	–	257 ± 22	65.0	30.7 ± 1.6	2.5	4.1
NaNO ₃ 8 mM	–	336 ± 4	105	95.1 ± 1.3	6.0	6.6
CH ₃ CO ₂ H 8 mM	194	603 ± 80	–	12.1 ± 0.7	3.5	4.3
HNO ₃ 5 mM; CH ₃ CO ₂ H 8 mM	197	495 ± 48	62.9	27.3 ± 1.5	2.4	3.7
NaNO ₃ 8 mM; CH ₃ CO ₂ H 8 mM	194	422 ± 5	101	57.2 ± 0.3	4.5	4.8
[P1888][TS]						
Pure water	–	14.8 ± 0.8	–	–	7.1	5.1
HNO ₃ 5 mM	–	24.6 ± 0.5	66.9	36.9 ± 1.1	2.4	2.7
NaNO ₃ 8 mM	–	31.2 ± 0.5	102	94.1 ± 3.2	5.8	6.0
CH ₃ CO ₂ H 8 mM	195	231 ± 7	–	–	3.5	3.6

anthranilic acid, which then passed to the aqueous phase, took place.

The leaching of [P1888][Ant] connected with the extraction of uranyl acetate showed a strong increase of the TOC value, while the TN value was in the same order of magnitude as for leaching to pure water. This was a hint for a significant contribution of ion exchange of the IL cation, i.e. UO_2^{2+} was taken up in the IL phase while [P1888] left (from the data in Table 5 the share of cation exchange could be estimated to around 70%). When extracting from a uranyl nitrate solution, the increase of the TOC value was much smaller, but the TN value decreased considerably compared to the reference value (i.e. the value before extraction). From these trends some form of neutral extraction of uranyl nitrate might be suggested. Table 4 shows that the amount of extracted nitrate to fully compensate for the total charge of extracted UO_2^{2+} via neutral extraction was exceeded in the extraction with [P1888][Ant], hinting at the possibility of nitric acid extraction (see also below).

Uranyl extraction using [P1888][TS] is accompanied by a change in the colour of the IL from yellow to dark red, irrespective of the uranyl counterion in the aqueous phase. Such colour shifts during uranyl extraction were observed before with ILs containing an anion which can be deprotonated and also with thiocyanate [16, 17]. We suppose that the deprotonation of the thiol group (see also the decrease in pH!) leads to formation of neutral or negatively charged uranyl thiosalicylate complexes ([P1888] stays in the IL phase as counterion). Similar extraction mechanisms were found by Biswas et al. [16] for trioctylmethylammonium hydrogen phthalate and by Egorov et al. [18] for trioctylmethylammonium salicylate. The most stable uranyl thiosalicylate complex would be $[\text{UO}_2(\text{TS})_2]^{2-}$ (i.e. two [TS] anions would bind to one uranyl cation), which would also explain the maximum loading capacity of 50 mol% given in Table 2. As this mechanism does not involve the aqueous anion, it is

surprising that the uranium loading capacity is only about half as large when nitrate is used. Here again extraction of nitric acid or nitrate, possibly in competition with metal extraction, was suggested, as the TN value declined during extraction while the pH stayed rather constant. Data in Table 6 show the ability of the investigated ILs to extract nitric acid.

Table 6 gives TOC, TN and pH data for shaking experiments of the ILs with water, HNO₃, NaNO₃ and CH₃COOH, respectively, but without uranyl. It can be seen that for both ILs the decrease of the TN was more pronounced when nitric acid was present in the aqueous phase compared to NaNO₃. The lower pH promoted the protonation of both IL anions as can be seen by the rise of pH (especially in the case of [P1888][Ant]). Free [P1888] cations may then be available for nitrate extraction, as was assumed already from the metal extraction data. Shaking [P1888][Ant] with a diluted acetic acid solution resulted in high TOC values, which means that leaching is substantial. When adding nitric acid or sodium nitrate to the acetic acid solution the leaching is suppressed, as we already saw in our results with uranyl nitrate and uranyl acetate solutions.

Conclusions

This paper gives an overview about radionuclide extraction from water samples by different ILs, with the main focus on uranium extraction. Generally, uranium was extracted with near to 100% yield by all investigated ILs, irrespective of feed solution pH. The same was true for ^{210}Po , the other radionuclides (^{234}Th , ^{226}Ra and ^{210}Pb), however, showed clearly lower extraction yields or were not extracted at all. Back-extraction with satisfying yield using diluted HNO₃ was only possible for uranium and the ILs [N1888][Ant], [N1888][C6SAC] and [PR4][ASA]. These ILs can then be

re-used while all other ILs had to be destroyed by concentrated acids for uranium recovery.

The time necessary for satisfying extraction was very short (10 min) for [P1888][C6SAc] and [N1888][Ant], while 60 and 150 min were needed by [N1888][C6SAc] and [P1888][Ant], respectively. Overnight shaking resulted in complete uranium extraction for all other investigated ILs. The maximum amount of uranium that can be taken up by the investigated ILs was generally very high and dependent of the uranyl counter-ion. For extractions from uranyl nitrate solutions the ILs showed loading capacities between 25 and 56 mol%, while from uranyl acetate solutions these values were clearly higher between 50 and 90 mol%.

Leaching of the IL to the aqueous phase was investigated thoroughly for the ILs [P1888][Ant] and [P1888][TS] by measuring the TOC and TN values as well as the pH in the aqueous phase before and after the extraction. This is very important with regard to the water quality after the radionuclide extraction step. As all of the investigated ILs with the exception of [P1888][TS] showed leaching values $> 1\%$ they cannot be used in drinking water processing but might be well suitable for technical applications.

From the leaching data some hints of the prevailing extraction mechanisms could be gained. Our findings suggested that at least 3 different processes as ion exchange, neutral extraction of uranyl nitrate and binding of uranyl by complexation were observed. This point will be the main focus of our future IL research.

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Compliance with ethical standards

Conflict of interest We have no conflict of interest to declare.

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