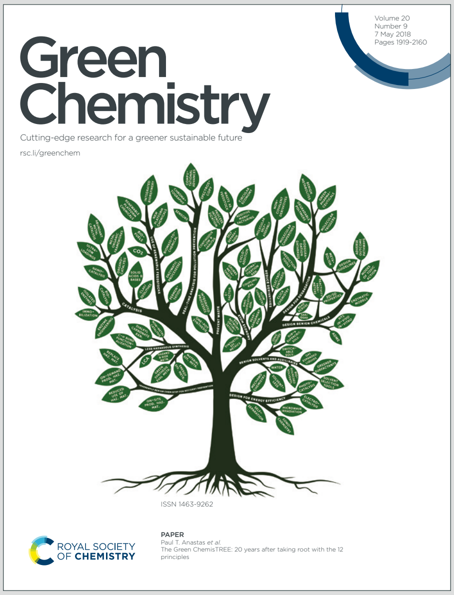
View Article Online
View Journal

Green Chemistry
Cutting-edge research for a greener sustainable future

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: S. Raiguel, W. Dehaen and K. Binnemans, *Green Chem.*, 2019, DOI: 10.1039/C9GC01626K.



ROYAL SOCIETY OF CHEMISTRY
rsc.li/greenchem

Manuscript for: Green Chemistry

View Article Online
DOI: 10.1039/C9GC01626K

# Isolation of molybdenum(VI) from simulated leachates of irradiated uranium-aluminum targets using diluted and undiluted sulfate ionic liquids

Stijn Raiguel[†], Wim Dehaen[†], Koen Binnemans[†]*

[†] KU Leuven, Department of Chemistry, Celestijnenlaan 200F, P.O. box 2404, B-3001 Leuven, Belgium.

*Corresponding author:

Email: Koen.Binnemans@kuleuven.be

## Abstract

View Article Online
DOI: 10.1039/C9GC01626K

A method is presented to separate molybdenum from other elements commonly present in oxidative alkaline leachates of irradiated uranium-aluminum targets for the production of molybdenum-99. The separation was accomplished by selective extraction of molybdate anions using triazolium and phosphonium sulfate ionic liquid extractants, either diluted in 1-octanol or undiluted. Molybdenum was then stripped from the organic phase using a sodium hydrogen carbonate solution. The extractant was regenerated by contacting the organic phase with an alkaline sulfate solution. The extraction mechanism and the influence of the diluent on the extractant performance were investigated. The reported method provides a promising alternative to state-of-the-art chromatographic processes, showing potential for limiting the production of radioactive waste.

Keywords: *green solvents; ionic liquids; hydrometallurgy; molybdenum; solvent extraction; technetium*

## Introduction

View Article Online
DOI: 10.1039/C9GC01626K

To date, $^{99m}$Tc is by far the most important diagnostic radionuclide in medicine, used in over 30 million procedures yearly.[1–3] It is particularly useful due to its short half-life of 6 hours, ideal γ-ray emission energy and rapid expulsion from the body, limiting the radiation dose to which the patient is exposed.[2–4] One major drawback associated with this short half-life is the difficulty of delivering this radionuclide to hospitals, as significant fractions of it will have decayed to its isomeric $^{99}$Tc daughter nuclide before a batch even reaches its destination. Therefore, batches are transported to hospitals as its parent nuclide, $^{99}$Mo, which has a much longer half-life of 66 hours.[3,4] The radiomolybdenum, present as $^{99}MoO_4^{2-}$, is adsorbed to an alumina column, which serves as a portable technetium generator. $^{99m}TcO_4^-$ can be eluted from this generator with physiological saline solution as it is formed by the decay of $^{99}$Mo.[2,3]

Currently, most radiomolybdenum is produced from irradiated, highly or low enriched uranium –aluminum alloy ($UAl_x$) targets.[1] As fission of uranium produces a wide array of elements as fission products, a rigorous purification process is required to isolate highly pure $^{99}$Mo from this mixture. Production centers involved in $^{99}$Mo purification each have a unique approach to the problem, of which the details are often kept highly secret. Most commonly, the purification occurs in acidic solutions. At Chalk River Laboratories (CRL) in Canada, formerly the largest production site worldwide for radiomolybdenum, dissolution of the targets in nitric acid was followed by a chromatographic purification on an alumina column.[5,6] An acid digestion is also employed at the Institute of Physics and Power Engineering (IPPE) in Russia, where the digestion is followed by a solvent extraction and a subsequent chromatographic purification in order to obtain the desired purity.[6–8] The Indonesian BATAN Institute uses the legacy CINTICHEM process for molybdenum purification, which consists of a dissolution step in $H_2SO_4$/$HNO_3$, followed by precipitation of iodide as silver(I) iodide and the sequestration of molybdenum by precipitation with α-benzoin oxime. The precipitate is then re-dissolved in sodium hydroxide and purified by chromatography.[7,9–11]

Other centers improve the selectivity of their leaching process by leaching under alkaline rather than acidic conditions. At IRE (Belgium), the target is dissolved in $NaOH/NaNO_3$, acidified and degassed to remove and recover iodine ($^{131}I$) and xenon ($^{133}Xe$). The process further comprises three chromatographic steps. The process employed by Mallinckrodt/ECN in the Netherlands entails alkaline digestion in sodium hydroxide without acidification. The digestion is followed by no fewer than five chromatographic steps. Similar strategies are also in use at INVAP (Argentina) and ANSTO (Australia).[7] AEC in South Africa also dissolves its targets in sodium hydroxide with the addition of a proper oxidizing agent, followed by three chromatographic steps.[6]

Several other procedures are described in literature and generally follow similar principles of leaching followed by chromatography. Some authors have reported modifications of the CINTICHEM process.[10,12–15] Other authors have explored various column materials to treat acidic $UAl_x$ leachates.[16–19] Another strategy that has received some attention is the exploitation of differences in the volatility of oxides and chlorides of the fission products. [20–23] Obviously, this also allows for very efficient removal of highly volatile iodine and xenon.

Chromatography is the most frequently used method for purification of acidic digests of irradiated $UAl_x$ targets in $^{99}Mo$ production.[7] Chromatography enables the production of high-purity samples from complex leachates, but consumes large quantities of chemicals and solvents. These materials are contaminated with radioactive isotopes in the process, implying that they must be treated as radioactive waste. The reagent consumption and waste production can be mitigated by moving towards a solvent-extraction-based procedure. In order to obtain pharmaceutical-grade purity of the final product, a highly selective solvent extraction procedure

View Article Online
DOI: 10.1039/C9GC01626K

is necessary. The radiochemical purity requirements are stipulated in the European, British and United States Pharmacopoeia and are expressed as activity ratios. Generally, radiochemical γ-impurities below $5 \cdot 10^{-5}$ are required per specified nuclide.[24]

The selectivity of the solvent extraction procedure can be aided by ensuring the leachate of the irradiated targets has the simplest possible chemical composition. Therefore, it is desirable to work with alkaline lixiviants, as uranium and many fission products (Ru, Zr, Nb, Ba, lanthanides, Am and Pu) do not dissolve under these conditions.[6,25,26] Furthermore, unreacted $^{235}$U is more easily recovered for reprocessing and recycling from alkaline solutions, as it remains in the solid residue.

Promising results were previously obtained by Al-Janabi *et al.*, who dissolved irradiated $U_3O_8$ in 6 mol $L^{-1}$ sodium hydroxide, followed by acidification of the leachate with sulfuric acid and extraction using di(2-ethylhexyl)phosphoric acid in hexane.[27] Tellurium and iodine were coextracted to significant extents, requiring a selective stripping of molybdenum using ammonia solution. Tellurium could be quantitatively scrubbed from the organic phase using brine, but iodine could not be removed. As such, the organic phase is not regenerated after the extraction procedure. A further drawback of this technique is that the leachate must be acidified prior to solvent extraction, resulting in a high consumption of acid required simply for the neutralization of the base used for leaching.

Some solvent extraction procedures for $^{99}$Mo perform well but require unacceptably dangerous reagents. Iqbal and Ejaz described a solvent extraction procedure comprising a solvent extraction of a HCl/KSCN leachate of the irradiated uranium product using 2-hexylpyridine in benzene, followed by stripping with 70% perchloric acid.[28] While selectivity for molybdenum over other metallic fission products and uranium was very high, nonmetallic fission products were not monitored in this study and the usage of highly oxidizing, concentrated perchloric acid

DOI: 10.1039/C9GC01626K

renders this procedure of little practical interest. A process that combines the technology of the CINTICHEM process with solvent extraction was developed by Nair *et al.*[29] Herein, ruthenium and iodine were first volatilized. α-Benzoin oxime was dissolved in ethyl acetate and used to extract molybdenum, which was then stripped by HCl/HF solution. The resulting final extract was purified by chromatography over Dowex® 1×8 anion exchange resin. The usage of HF is a major drawback of this procedure.

In this paper, we describe a method to isolate molybdenum from a simulated alkaline leachate of irradiated $UAl_x$ targets entirely *via* solvent extraction with sulfate ionic liquids as extractants. Performing solvent extraction directly on an alkaline leachate is challenging. Metals are present as anionic complexes in alkaline media. Hence, anion exchanging extractants are required. These are generally quaternary ammonium or phosphonium salts, which are known to decompose in contact with strong bases.[30–33] Work by Lethesh *et al.* describes base-stable quaternary ammonium salts with 2-ethylhexyl side chains to prevent the cation from decomposing *via* the Hoffman elimination. However, the compounds were found to be very hydrophilic, leading to losses of extractant to the aqueous phase.[32] Some imidazolium salts also exhibit good resistance against strong bases.[34,35] We opted to investigate two extractants. The first is a long-chain phosphonium extractant (trihexyltetradecylphosphonium sulfate), analogs of which have been proven to be compatible with moderately strong alkalis.[36] The second is an extractant based on the 1,2,3-triazolium cation (4-ethyl-1,3-bis(2-ethylhexyl)-5-propyl-1,2,3-triazolium sulfate), which can conveniently be prepared on a larger scale. A sulfate system was chosen as the strongly hydrophilic sulfate anion can readily be exchanged for dianionic molybdate ($MoO_4^{2-}$). We also demonstrate that the phosphonium extractant is suitable for use without diluent, *i.e.* as an ionic liquid. The advantage of the latter approach is a mitigation of the health and safety risks typically associated with the use of organic solvents, due to the negligible room-temperature vapor pressure of ionic liquids.[37,38]

## Experimental

View Article Online
DOI: 10.1039/C9GC01626K

### *Chemicals*

2-Ethylhexylamine (99%), triethylamine (99%), 1-hexanol (98%), 1-octanol (99%), NaOD (40 wt% in $D_2O$, 99 atom% D), sodium periodate (99%), sodium aluminate (technical grade) and sodium azide (99%) were purchased from Acros Organics (Geel, Belgium). Sodium dihydrogen phosphate (anhydrous, 98%), heptane (mixture of isomers, 99%), 4-aminobenzoic acid (99%), molybdenum standard solution (1000 ppm), aluminum standard solution (1000 ppm) and molybdenum standard oil solution (1000 ppm) were purchased from Chem-Lab (Zedelgem, Belgium). 4-Heptanone (99%) was purchased from Alfa Aesar (Karlsruhe, Germany). Ammonia (25 wt% in water), sodium hydrogen carbonate (analytical reagent grade), ethyl acetate (technical grade), toluene (reagent grade), magnesium sulfate (dried), sodium sulfate (analytical reagent grade) and sodium hydroxide (analytical grade) were purchased from VWR (Oud-Heverlee, Belgium). Chloroform-d ($CDCl_3$, 99.8 atom% D), mesyl chloride (98%), cesium hydroxide monohydrate (99.95%) and sodium molybdate dihydrate (99+ %) were purchased from Sigma-Aldrich (Overijse, Belgium). Telluric acid was purchased from TCI (Zwijndrecht, Belgium). Cobalt standard oil solution (5000 ppm) was purchased from PerkinElmer (Zaventem, Belgium). Lithium sulfate (high purity) was purchased from UCB (Brussels, Belgium). All reagents were used as received, without further purification.

### *Instrumentation*

$^{1}H$ NMR spectra were recorded on a Bruker Avance 300 spectrometer operating at 300 MHz. $^{13}C$, $^{31}P$ and quantitative $^{1}H$ NMR spectra were recorded on a Bruker Avance II 400 spectrometer operating at 100 MHz for $^{13}C$, 162 MHz for $^{31}P$ and 400 MHz for $^{1}H$. Samples for $^{1}H$ and $^{13}C$ NMR were diluted in $CDCl_3$ and internally referenced to tetramethylsilane. Samples for $^{31}P$ NMR were diluted in $CDCl_3$ and externally referenced to 10 wt% $H_3PO_4$ in $D_2O$. $^{95}Mo$

View Article Online
DOI: 10.1039/C9GC01626K

NMR spectra were recorded on a Bruker Avance 600 spectrometer equipped with a 10 mm probe and operating at 39 MHz. Samples were measured undiluted and externally referenced to 200 mg $L^{-1}$ $Na_2MoO_4 \cdot 2H_2O$ in water. The Spinworks 4.2.8 and Mesternova 6.0.2 software packages were used in the analysis of nonmetal and metal NMR spectra, respectively. A polynomial baseline correction was applied to the $^{95}Mo$ spectra.

FTIR spectra were recorded in ATR mode on a Bruker Vertex 70 infrared spectrometer equipped with a platinum ATR module and a diamond sample crystal. Mass spectra were recorded on a Finnigan LCQ Advantage electrospray ionization ion trap mass spectrometer. Viscosities were measured on an Anton Paar Lovis 2000M/ME combined densitometer-rolling ball viscometer. Densities of water-saturated ionic liquids were also measured using this device. Densities of pure ionic liquids were measured by pycnometry due to their high viscosity. The water content of organic samples was determined by Karl Fischer titrimetry, performed on a Mettler-Toledo C30S coulometric titrator. To facilitate sample injection, a measured mass of the organic sample was dissolved in 1 mL of dry DMSO before injection. A blank measurement of 1 mL of dry DMSO was also recorded. The water content of the blank was then subtracted from the measured water content of the sample solution in order to obtain the actual water content of the organic sample. Water used for analysis was always of ultrapure quality (resistivity 18.2 MΩ cm at 25 °C), provided by a Millipore Milli-Q Reference A+ system.

*Quantitative NMR*

The organic content of the aqueous phase was determined using quantitative $^1H$ NMR. Spectra were recorded on a Bruker Ascend 400 spectrometer operating at 400 MHz. A recycle delay (d1) time of 3 s was applied for a total of 32 scans per sample. Samples were prepared by contacting a 100 mg aliquot of the extractant with 1 mL of a $D_2O$ sample with an appropriate concentration of NaOD. Subsequently, 10 μL of methanol was added to 500 μL of the $D_2O$ solution as internal standard. The extractant concentration of the aqueous solution was

View Article Online
DOI: 10.1039/C9GC01626K

determined from the relative integrals of the methanol $CH_3$ signal and the upfield signals of the hydrocarbon chains of the extractants. A phase and baseline correction was applied to obtain a more accurate estimate of the organic content of dilute samples.

*ICP-OES*

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used for the analysis of molybdenum and aluminum. Aqueous phase samples were prepared by diluting 100 µL of the analyte solution to 10 mL with 2 vol% $HNO_3$ in ultrapure water. Scandium standard solution (1 ppm final concentration) was added as internal reference. Calibration curves for molybdenum and aluminum were constructed using an external standard series. Analyses of aqueous samples were carried out on a PerkinElmer Optima 8300 spectrometer equipped with a GemTip Cross-Flow II nebulizer, Scott double-pass spray chamber, alumina injector and PerkinElmer Hybrid XLT ceramic-quartz torch. The radial viewing mode was used for all measurements. The line at 202.031 nm was used for the determination of molybdenum, while the line at 396.152 nm was used for aluminum. These wavelengths were selected on their performance in the measurement of samples with known concentrations. Samples were measured in triplicate.

Samples of the organic phase were prepared by diluting a 50 µL aliquot of the organic phase to 5 mL with 1-octanol. Cobalt standard oil solution (10 ppm final concentration) was added as internal reference. An external standard series, prepared using molybdenum standard oil solution, was used to construct the calibration curves. Organic samples were analyzed using a PerkinElmer Avio 500 spectrometer equipped with a GemCone Low-Flow Nebulizer, baffled cyclonic spray chamber, alumina injector and PerkinElmer Hybrid XLT Organics torch. The line at 202.031 nm was measured in radial viewing mode for the determination of molybdenum.

View Article Online
DOI: 10.1039/C9GC01626K

This wavelength was selected on its performance in the measurement of samples with known concentrations. Samples were prepared in duplicate, each measured in triplicate.

*TXRF*

Iodine cannot be reliably quantized *via* ICP-OES devices due to its low emission intensity, while the speciation of cesium in ICP-OES devices is too variable to allow accurate determination. Therefore, these elements were determined using total reflection X-ray fluorescence (TXRF) spectroscopy on a Bruker S2 Picofox benchtop TXRF spectrometer. Samples for TXRF were prepared by first diluting 30 μL of the solution to be analyzed to 1000 μL with a solution containing Triton® X-100 (5 vol%) and $HNO_3$ (5 vol%) in ultrapure water. Cerium standard solution (30 ppm Ce as final concentration) was added as internal standard. Triton® X-100 ensures a homogeneous sample distribution after drying (*vide infra*) while $HNO_3$ prevents base-induced precipitation of the Ce standard.

A 2 μL aliquot of the sample solution was pipetted onto a quartz carrier, previously pretreated with a silicone solution in isopropanol (Serva electrophoresis, Heidelberg, Germany) to prevent spreading of the droplet. The carrier was then dried for 30 min at 60 °C and subsequently analyzed with the X-ray source operating at 50 kV and 600 μA. Samples were measured for 1200 seconds each. Samples were prepared and analyzed in triplicate, to account for possible inhomogeneity in the sample morphology. Relative standard deviations on the calculated concentrations were generally about 1–10%, depending on the salt concentration of the sample and its concentration (higher relative standard deviations mostly at high percentages extraction, when the raffinate is very dilute).

*Solvent extraction*

Appropriate dilutions of the extractants in the required diluent were made. The organic phase was presaturated with a blank NaOH solution by shaking vigorously and subsequently centrifuging to disengage the two phases. The employed NaOH concentration was identical to that of the aqueous phase used for solvent extraction. A 500 μL aliquot of the organic layer was taken and combined with 1.000 mL of the aqueous feed solution. The vial containing both phases was then shaken for 30 minutes using an Allsheng TMS-300 Thermo Shaker. The vials were shaken in the vertical position at 30 °C and 3000 rpm. After shaking, phase disengagement was expedited by centrifuging using a Heraeus Labofuge 200. Samples of the aqueous phase were used for further analysis.

Using concentration data for the aqueous phase before and after extraction, the percentage extraction was calculated using Eq. 1:

$$\%E = \frac{c_{aq,\,i} - c_{aq,\,f}}{c_{aq,\,i}} \cdot 100\% \tag{1}$$

The distribution ratio was calculated using Eq. 2:

$$D = \frac{c_{org,\,f}}{c_{aq,\,f}} = \frac{(c_{aq,\,i} - c_{aq,\,f}) \cdot V_{aq}}{c_{aq,\,f} \cdot V_{org}} \tag{2}$$

Where $c_{org}$ and $c_{aq}$ indicate organic and aqueous phase concentrations, respectively. Subscripts $i$ and $f$ respectively denote initial (before extraction) and final (after extraction) values. $V_{org}$ and $V_{aq}$ are the organic and aqueous phase volumes.

*Stripping*

The loaded organic phase used in stripping experiments was prepared by contacting 2.00 mL of the extractant or an appropriate dilution thereof with 4.00 mL of a solution containing $Na_2MoO_4$ (1000 ppm Mo) and NaOH (2.00 mol $L^{-1}$). The samples were shaken for 30 minutes in centrifuge tubes using a Burrell Scientific Wrist-Action Shaker. Phase separation was expedited by centrifuging using a Heraeus Labofuge 200.

A stripping liquor solution was prepared by dissolving 1.00 mol $L^{-1}$ sodium hydrogen carbonate in ultrapure water. A 500 μL aliquot of the loaded organic phase was then contacted with 2.00

View Article Online
DOI: 10.1039/C9GC01626K

mL of the stripping liquor for 30 minutes at 30 °C in an Allsheng TMS-300 Thermo Shaker, operating at 3000 rpm. Phase separation was expedited using a Heraeus Labofuge 200. The organic phase before and after stripping was analyzed by ICP-OES.

The percentage stripping was calculated according to Eq. 3:

$$\%S = \frac{c_{org,\ i} V_{org,i} - c_{org,\ f} V_{org,f}}{c_{org,\ i} V_{org,i}} \cdot 100\% \qquad (3)$$

The final phase volume was determined by measurement of the density and the water content of the organic phase before and after stripping (see ESI page S15). When diluted extractants were used, phase volume changes upon stripping were negligible, allowing the simplified Eq. 4 to be used.

$$\%S = \frac{c_{org,\ i} - c_{org,\ f}}{c_{org,\ i}} \cdot 100\% \qquad (4)$$

The distribution ratio under stripping conditions is calculated according to Eq. 2.

## Results and discussion

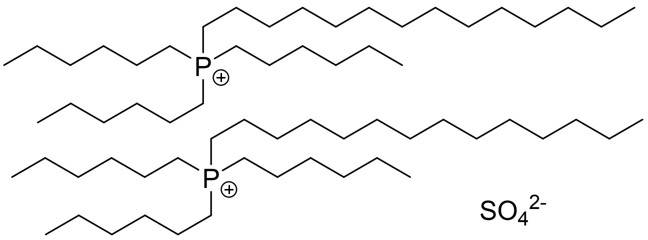
### *Synthesis and characterization of the ionic liquid extractants*

Trihexyltetradecylphosphonium sulfate, $[P_{66614}]_2[SO_4]$, was prepared from commercial Cyphos® IL 101 by an anion metathesis reaction with aqueous $NaHSO_4$ followed by treatment with aqueous NaOH. The product is a deliquescent solid at room temperature which melts into a highly viscous liquid in the range of 28–34 °C.

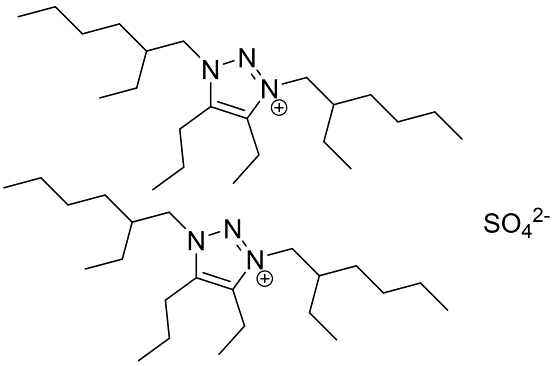
4-Ethyl-1,3-bis(2-ethylhexyl)-5-propyl-1,2,3-triazolium sulfate, $[EhEhT_{23}]_2[SO_4]$, was synthesized using a method reported previously.[39] This method entailed the synthesis of the precursor, 4-ethyl-1-(2-ethylhexyl)-5-propyl-1,2,3-triazole, from 4-heptanone, 2-ethylhexylamine and 4-azidobenzoic acid. Subsequently, this precursor was quaternized using 2-ethylhexyl methanesulfonate. The methanesulfonate salt was then converted to the

View Article Online
DOI: 10.1039/C9GC01626K

corresponding sulfate salt by an anion metathesis reaction with aqueous $NaHSO_4$, followed by treatment with an aqueous NaOH solution. Full synthetic procedures and characterization data of both extractants are provided in the Electronic Supplementary Information (page S2-S4). The structures of both extractants are shown in Fig. 1.



$[P_{66614}]_2[SO_4]$



$[EhEhT_{23}]_2[SO_4]$

*Fig. 1: Structures of the extractants used in this work.*

The physicochemical properties of the extractants were determined and are summarized in Table 1. Both compounds melt well below 100 °C and can thus be considered ionic liquids.[37,38] $[P_{66614}]_2[SO_4]$ melts above room temperature, in the range of 28–34 °C. By contrast, $[EhEhT_{23}]_2[SO_4]$ remains liquid even after prolonged storage at room temperature. This reduction in melting point is presumed to result from the high degree of charge delocalization in the triazolium cation. Whilst the high charge of the sulfate dianion causes the dry ionic liquids to be very viscous, it also induces the uptake of large amounts of water in solvent extraction systems, reducing their viscosity to more practical levels. When saturated with water, both compounds remained liquid at room temperature, allowing them to be used in diluent-free extraction systems. The viscosity of $[EhEhT_{23}]_2[SO_4]$ is markedly lower than that of the phosphonium ionic liquid, once again a presumed result of the charge delocalization of the aromatic cation.

The mutual miscibility of both phases is an important factor determining the efficacy of solvent extraction systems. $[P_{66614}]_2[SO_4]$ is poorly soluble even in pure water due to its highly hydrophobic cation, with a solubility of about 0.63 wt%. $[EhEhT_{23}]_2[SO_4]$ is miscible with pure water. Upon addition of 2.00 mol $L^{-1}$ of NaOH to the aqueous phase, $[EhEhT_{23}]_2[SO_4]$ formed an aqueous biphasic system. However, due to the high mutual miscibility of both phases, $[EhEhT_{23}]_2[SO_4]$ should be diluted with an organic solvent for use in solvent extraction (*vide infra*). The equilibrium concentration of water in the organic phase remains high even in contact with 2.00 mol $L^{-1}$ NaOH: nearly 27 wt% for $[P_{66614}]_2[SO_4]$ and 50 wt% for $[EhEhT_{23}]_2[SO_4]$. While remarkable, this does not impede the use of the undiluted ionic liquids in solvent extraction systems.

View Article Online
DOI: 10.1039/C9GC01626K

Table 1: Physicochemical properties of the extractants.

| | $[P_{66614}]_2[SO_4]$ | $[EhEhT_{23}]_2[SO_4]$ |
|---|---|---|
| Melting point range (° C) | 28-34 °C | RTIL[a] |
| Density[b] (g cm$^{-3}$) | 0.907 | 0.967 |
| Dynamic viscosity, dry[c] (cP) | 7705 at 50 °C | 798 at 50 °C<br>4135 at 30 °C |
| Dynamic viscosity, water saturated[d] (cP) | 90 | 14 |
| Solubility in water (wt%) | 0.63 | miscible |
| Decomposition temperature[e] (°C) | 244 | 154 |

[a] Room temperature ionic liquid
[b] At 30 °C
[c] Residual water content: 0.29 wt% for $[P_{66614}]_2[SO_4]$, 0.83 wt% for $[EhEhT_{23}]_2[SO_4]$
[d] At 30 °C, in equilibrium with 2.00 mol L$^{-1}$ NaOH
[e] Onset point at a ramp rate of 3 °C min$^{-1}$

1-Octanol was chosen as diluent for solvent extraction studies due to its relatively high flash point, high hydrophobicity, good biodegradability and miscibility with the extractants.[40] The losses of extractant to the aqueous phase under realistic extraction conditions were determined by quantitative $^1$H NMR. Undiluted $[P_{66614}]_2[SO_4]$ displayed a solubility in 2.00 mol L$^{-1}$ NaOH of 390 ppm. Losses of $[P_{66614}]_2[SO_4]$ from a 40 vol% solution in 1-octanol to 2.00 mol L$^{-1}$ NaOH in 1:1 phase volume ratio result in an aqueous $[P_{66614}]_2[SO_4]$ concentration of 206 ppm. In a similar system with $[EhEhT_{23}]_2[SO_4]$, an extractant concentration of 268 ppm was found. This value increases to 738 ppm when the aqueous phase contains 1 mol L$^{-1}$ of NaOH, a concentration more suitable for extraction using this extractant (*vide infra*).

The stability of the extractants under extraction conditions was evaluated over extended periods of time. Samples were prepared by contacting an aliquot (approx. 50 µL) of the ionic liquid with 1 mL of 2.00 mol L$^{-1}$ NaOH at the specified conditions. Subsequently, organic material was extracted into 1 mL of chloroform-d. The degree of decomposition of the triazolium extractant $[EhEhT_{23}]_2[SO_4]$ was determined using $^1$H NMR. Our earlier research has showed

DOI: 10.1039/C9GC01626K

that 1,2,3-triazolium ionic liquids decompose to 1,2,3-triazoles in alkaline solutions.[39] The degree of decomposition could thus be determined by integration of the ionic liquid and triazole signals. $[EhEhT_{23}]_2[SO_4]$ showed excellent resistance to base-induced decomposition at 2.00 mol $L^{-1}$ NaOH. After 10 days of continuous exposure to 2.00 mol $L^{-1}$ NaOH at 60 °C, only 2 mol% of the extractant was found to have decomposed.

The stability of the phosphonium extractant $[P_{66614}]_2[SO_4]$ was determined using $^{31}P$ NMR. Phosphonium salts are known to decompose to phosphine oxides in alkaline solutions.[30,31,33] In 2.00 mol $L^{-1}$ NaOH at 60 °C, 84 mol% of the $[P_{66614}]_2[SO_4]$ had decomposed to phosphine oxides after 10 days. At 30 °C, the percentage of decomposition drops to 10 mol% over 10 days of contact with 2.00 mol $L^{-1}$ NaOH. Evidently, the recyclability of the triazolium extractant is far superior to that of the phosphonium-based extractant, and prolonged usage of the latter will require precautions against radiation-induced heating during contact with the alkaline feed solution. The NMR spectra of the extractants after contact with the alkaline solutions can be found in the ESI (Fig. S4, S9 and S10). Note that the triazolium extractant dissolved into the aqueous phase under the conditions used for this experiment.

*Mechanistic studies*

$^{95}Mo$ NMR and infrared spectroscopy were used to determine the speciation of molybdenum in the organic phase. $^{95}Mo$ NMR spectra were externally referenced to a 200 g $L^{-1}$ solution of $Na_2MoO_4 \cdot 2H_2O$ in water. Spectra were recorded of pure $[P_{66614}]_2[SO_4]$, 40 vol% $[P_{66614}]_2[SO_4]$ in 1-octanol, 20 vol% $[P_{66614}]_2[SO_4]$ in 1-octanol and pure $[EhEhT_{23}]_2[SO_4]$. All samples were presaturated with a blank 2.00 mol $L^{-1}$ NaOH solution and then loaded from a 200 g $L^{-1}$ solution of $Na_2MoO_4 \cdot 2H_2O$ in water containing 2.00 mol $L^{-1}$ NaOH (organic to aqueous phase volume ratio: 2:5). In spite of the very large chemical shift range of $^{95}Mo$, the sample signal of the organic phase species was never shifted further than 10 ppm downfield from the reference signal. These small downfield shifts can simply be attributed to solvent and dilution effects.

View Article Online
DOI: 10.1039/C9GC01626K

Much larger changes in chemical shift are expected should speciation changes occur upon extraction, for instance the oligomerization of molybdate anions. The obtained chemical shift values thus demonstrate that molybdenum is extracted as $MoO_4^{2-}$, the same species that exists in the aqueous phase. Furthermore, the narrow linewidth observed in all spectra is in agreement with the high $T_d$ symmetry of the $MoO_4^{2-}$ anion. All sample spectra are shown in Fig. 2.

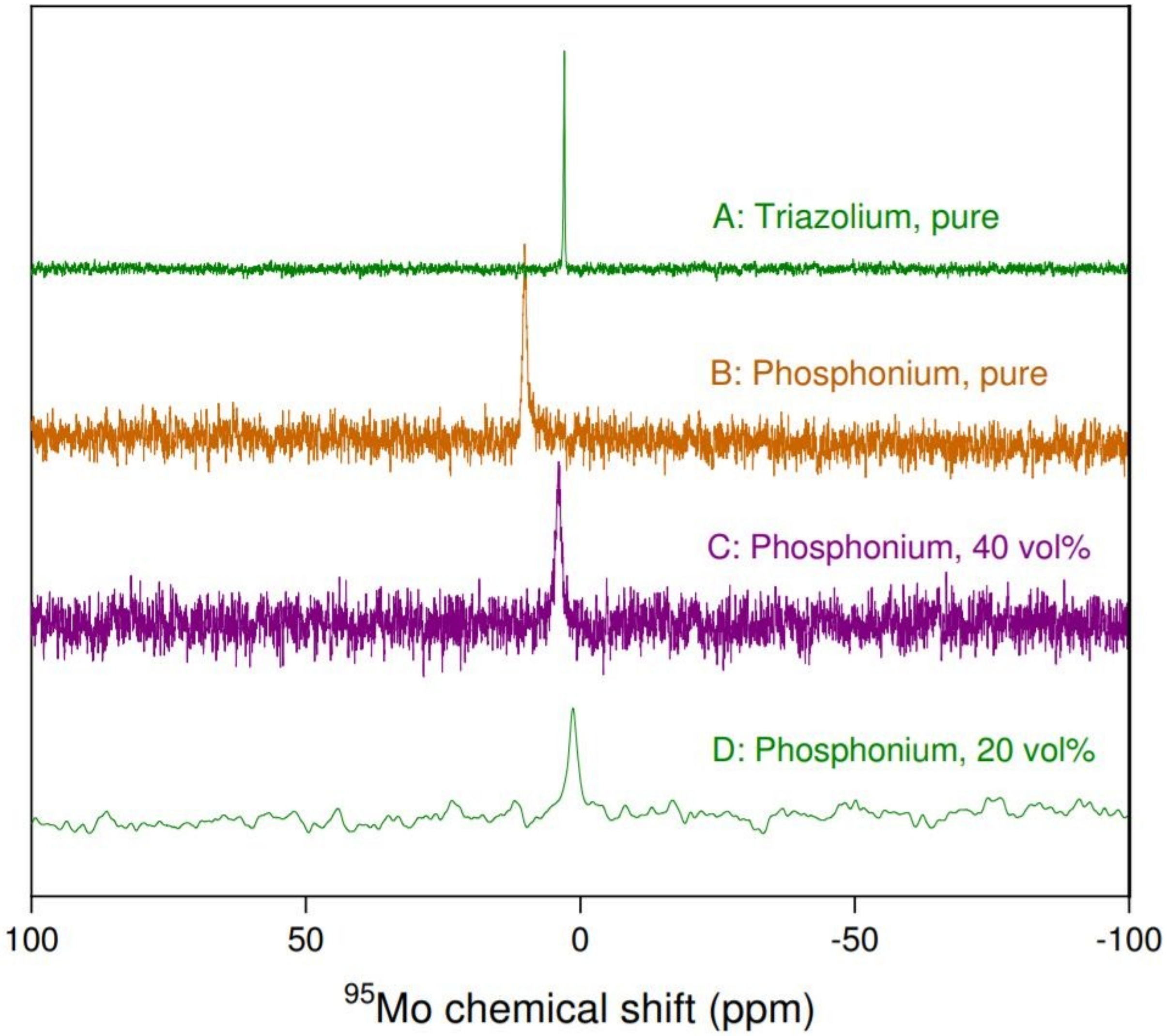


*Fig. 2: $^{95}$Mo NMR spectra of (A) loaded, undiluted $[EhEhT_{23}]_2[SO_4]$, (B) loaded, undiluted $[P_{66614}]_2[SO_4]$, (C) loaded 40 vol% $[P_{66614}]_2[SO_4]$ diluted in 1-octanol and (D) loaded 20 vol% $[P_{66614}]_2[SO_4]$ diluted in 1-octanol. All spectra are referenced to 200 g $L^{-1}$ $Na_2MoO_4 \cdot 2H_2O$ in water, set to 0 ppm.*

The above findings were corroborated by infrared spectroscopy of the loaded organic phases. Sulfate and molybdate anions, being structurally analogous and isoelectronic, both display

View Article Online
DOI: 10.1039/C9GC01626K

strong absorption bands in their infrared spectra attributed to their asymmetric stretching modes.[41–43] The molybdate band appears at lower wave numbers (approximately 800−820 $cm^{-1}$) than the sulfate band (approximately 1060-1080 $cm^{-1}$) as a result of the greater atomic mass of molybdenum and the comparatively weaker Mo=O bond. These bands can be used to detect presence of either anion and can clearly be seen in the spectra of pure $[P_{66614}]_2[SO_4]$ and $Na_2MoO_4 \cdot 2H_2O$. $[P_{66614}]_2[SO_4]$ that was maximally loaded with molybdenum displays a strong molybdate asymmetric stretching band, but lacks the corresponding sulfate signal. Hence, sulfate is exchanged for molybdate in the organic phase during extraction. Moreover, this implies that the fully loaded extractant can be viewed as the ionic liquid $[P_{66614}]_2[MoO_4]$. The spectra before and after loading are shown and compared in Fig. 3.

View Article Online
DOI: 10.1039/C9GC01626K

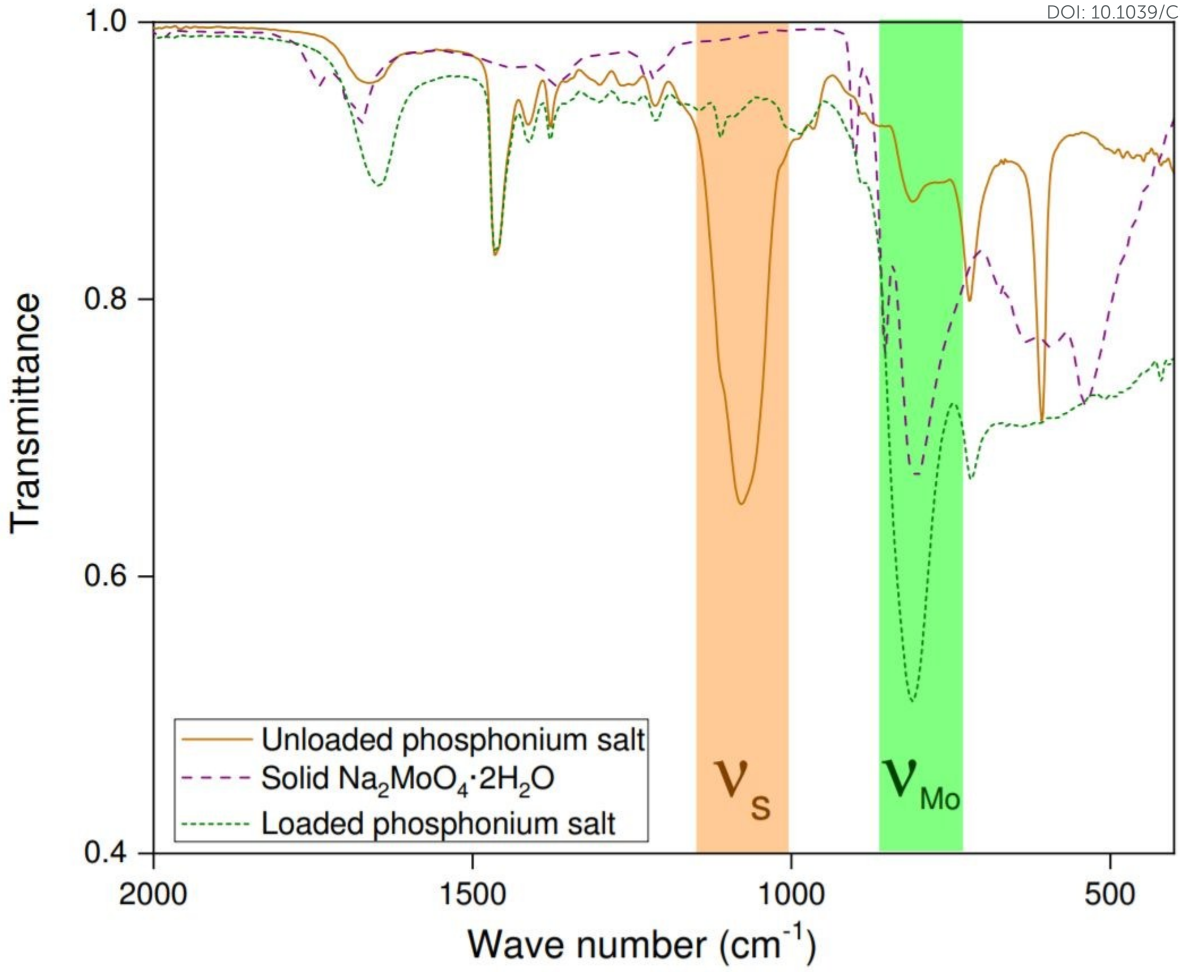


*Fig. 3: Comparison of the infrared spectra of loaded and unloaded $[P_{66614}]_2[SO_4]$ and solid $Na_2MoO_4{\cdot}2H_2O$. The sulfate and molybdate stretching bands are highlighted and respectively labeled as $\nu_S$ and $\nu_{Mo}$. Loading was accomplished by contacting the organic phase with a 200 g $L^{-1}$ solution of $Na_2MoO_4{\cdot}2H_2O$ containing 2.00 mol $L^{-1}$ NaOH in 2:5 volume ratio.*

View Article Online
DOI: 10.1039/C9GC01626K

Similarly, when $[EhEhT_{23}]_2[SO_4]$ was loaded with molybdenum, the molybdate band appeared in the spectrum. Due to the high water content of the loaded organic phase, background absorption prevents clear evaluation of the intensity of the sulfate absorption band. Regardless, the infrared spectra of loaded and unloaded 50 wt% $[EhEhT_{23}]_2[SO_4]$ in 1-octanol do show a striking attenuation of the sulfate absorption band upon loading. The spectra before and after loading are shown and compared in Fig. 4.

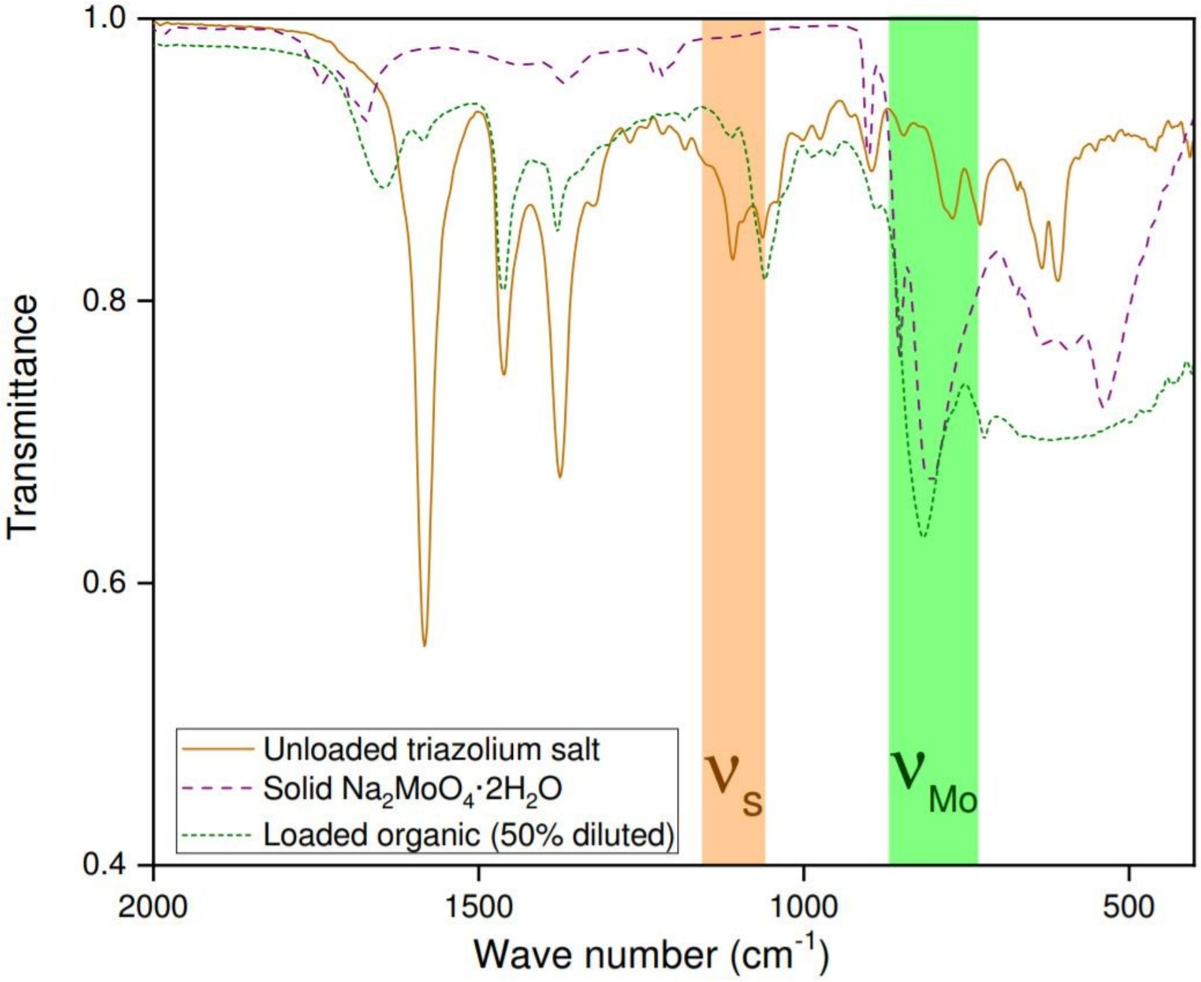


*Fig. 4: Comparison of the infrared spectra of loaded and unloaded $[EhEhT_{23}]_2[SO_4]$ (50 vol% diluted in 1-octanol) and solid $Na_2MoO_4 \cdot 2H_2O$. The sulfate and molybdate stretching bands are highlighted and respectively labeled as $\nu_S$ and $\nu_{Mo}$. Loading was accomplished by contacting the organic phase with a 200 g $L^{-1}$ solution of $Na_2MoO_4 \cdot 2H_2O$ containing 2.00 mol $L^{-1}$ NaOH in 2:5 volume ratio.*

Based upon the aforementioned $^{95}$Mo NMR and infrared spectra, an extraction mechanism can be inferred in which sulfate anions in the organic phase is replaced by molybdate anions from the aqueous phase. The proposed extraction mechanism is thus an anion-exchange process, which is expected to be favorable due to the larger ionic radius of the molybdate anion with respect to that of the sulfate anion. This difference in radius leads to a lower charge density and thus comparatively weaker hydration of the molybdate anion. As a result, the transfer of sulfate anions to the aqueous phase in exchange for molybdate anions is favorable. Such phenomena were studied and discussed in detail by Dupont et al.[44] The process can be represented by the following reaction equation:

$$\overline{[\mathrm{Q}]_2[\mathrm{SO}_4]} + \mathrm{MoO}_4^{2-} \rightleftharpoons \overline{[\mathrm{Q}]_2[\mathrm{MoO}_4]} + \mathrm{SO}_4^{2-} \tag{4}$$

In which Q denotes the organic cation of the extractant and an overbar denotes species in the organic phase.

*Diluent and cation effects*

The infrared spectra of undiluted $[\mathrm{EhEhT}_{23}]_2[\mathrm{SO}_4]$ and $[\mathrm{P}_{66614}]_2[\mathrm{SO}_4]$ show marked differences in their sulfate ν-regions. The sulfate ($\nu_\mathrm{S}$) band is shifted to higher wave numbers in $[\mathrm{EhEhT}_{23}]_2[\mathrm{SO}_4]$ with respect to $[\mathrm{P}_{66614}]_2[\mathrm{SO}_4]$ (1109 *vs.* 1079 $\mathrm{cm}^{-1}$), as can be seen in Fig. 5. The $\delta_\mathrm{S}$-band is located at approximately the same wave number in both compounds. One can thus conclude that significant differences exist in the coordination of the sulfate anion to cations in the pure extractants.

The use of a diluent also affects the solvation of the sulfate anion. When $[\mathrm{P}_{66614}]_2[\mathrm{SO}_4]$ is diluted in 1-octanol, the sulfate asymmetric stretch ($\nu_\mathrm{S}$) band is shifted from 1079 to 1059 $\mathrm{cm}^{-1}$. Furthermore, the bending mode ($\delta_\mathrm{S}$) band, which is prominently present at 607 $\mathrm{cm}^{-1}$ in undiluted $[\mathrm{P}_{66614}]_2[\mathrm{SO}_4]$, is shifted to 619 $\mathrm{cm}^{-1}$ and nearly completely absent from the diluted sample (Fig. 5). Both are evidence of solvation of the sulfate anion in diluted $[\mathrm{P}_{66614}]_2[\mathrm{SO}_4]$, which is not present in the pure extractant.[42,45,46] The lack of sulfate solvation in the latter can be attributed to the tetrahedral structure of the cation, in which polarized protons and the positively charged

View Article Online
DOI: 10.1039/C9GC01626K

core are sterically shielded by the alkyl substituents. Further evidence of hydrogen bonding between 1-octanol and the sulfate anion in $[P_{66614}]_2[SO_4]$ is presented in the electronic supplementary information (Fig. S5), where $^1$H NMR spectra show the disappearance of the hydroxyl proton signal upon addition of $[P_{66614}]_2[SO_4]$, which again indicates the presence of rapidly exchanging hydrogen bonds.

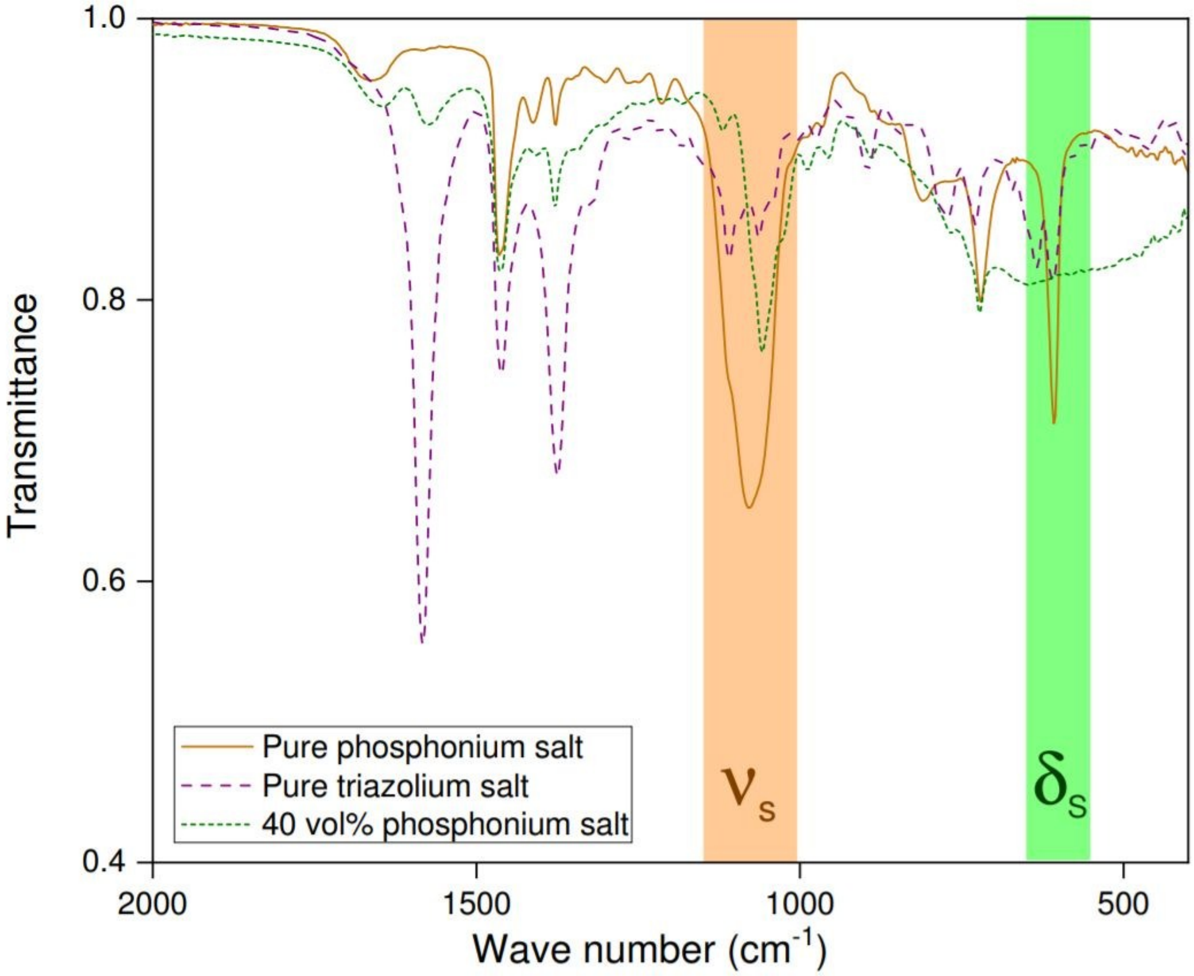


*Fig. 5: Comparison of the infrared spectra of $[P_{66614}]_2[SO_4]$, $[EhEhT_{23}]_2[SO_4]$ and 40 vol% $[P_{66614}]_2[SO_4]$ diluted in 1-octanol. The sulfate asymmetric stretching and bending bands are highlighted and respectively labeled as $\nu_S$ and $\delta_S$.*

The effect of the diluent on the solvation of the extractant is clearly reflected in the distribution ratios observed for molybdenum. Fig. 6 shows the distribution ratio for molybdenum ($D_{Mo}$) as a function of the extractant concentration for $[P_{66614}]_2[SO_4]$ dissolved in 1-octanol and toluene, and for $[EhEhT_{23}]_2[SO_4]$. The indicated volume fractions denote the ratio of the extractant to the total dry volume of the organic phase. Upon saturation with water, the volume fraction of the extractant thus decreases further. The results shown in Fig. 6 reveal a very strong dependence of $D_{Mo}$ on the extractant concentration. Ideally, the logarithms of both $D_{Mo}$ and the extractant concentration are expected to correlate linearly with a slope of 1 as a result of the equilibrium of Equation (4) being shifted to completion. A negative deviation from this trend can be expected at higher extractant concentrations due to the uptake of large amounts of water, which diminishes the difference in solvation experienced by solutes upon phase transfer. However, the dependence of $D_{Mo}$ on the concentration of $[P_{66614}]_2[SO_4]$ was far stronger than predicted for an ideal system, particularly at low extractant concentrations. This can be correlated to the aforementioned infrared and NMR studies, which show increased solvation of the sulfate anion in 1-octanol with respect to the pure extractant. Thus, increasing the extractant concentration not only increases the amount of sulfate available to drive Eq. 4 to higher values of $D_{Mo}$, but also decreases the solvation of the sulfate anions, thus further increasing their activity. No such effect was observed for $[P_{66614}]_2[SO_4]$ in toluene, where no strong hydrogen bonding can take place. The observed values for $D_{Mo}$ in this system are more or less constant, regardless of the extractant concentration, which may result from the competing effects of the increased concentrations of extractant and water in the organic phase.

$[EhEhT_{23}]_2[SO_4]$ exhibits much less affinity for molybdenum than $[P_{66614}]_2[SO_4]$. The lower observed values of $D_{Mo}$ are likely related to the higher hydrophilicity of $[EhEhT_{23}]_2[SO_4]$, leading to a much higher uptake of water. Furthermore, differences in solvation of the sulfate anion could also be involved, as the strong dependence of $D_{Mo}$ on the extractant concentration in 1-octanol was not observed in for the triazolium extractant. This can again be correlated to the abovementioned infrared spectra, which indicate significant differences in solvation of the sulfate anions in both undiluted extractants.

View Article Online
DOI: 10.1039/C9GC01626K

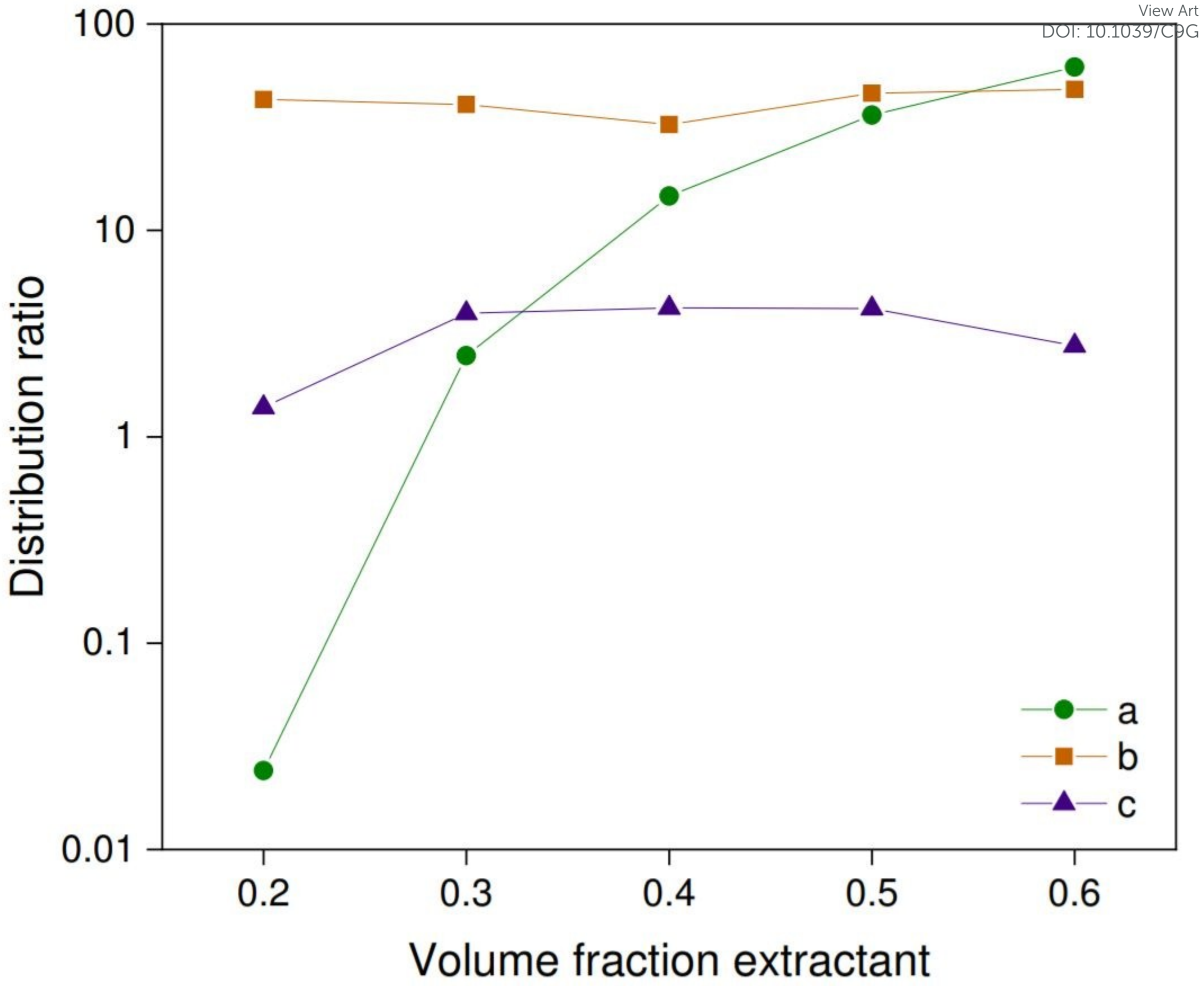


*Fig. 6: Variation of the distribution ratio of molybdenum as a function of the extractant concentration. The aqueous feed was a 1000 ppm solution of $Na_2MoO_4$ in 1.00 mol $L^{-1}$ NaOH. The organic phases were $[P_{66614}]_2[SO_4]$ in 1-octanol (a) $[P_{66614}]_2[SO_4]$ in toluene (b) and $[EhEhT_{23}]_2[SO_4]$ in 1-octanol (c). The organic phases were presatured with 1.00 mol $L^{-1}$ NaOH. A phase ratio of 2:1 (aqueous to organic) was used at 30 °C.*

### *Separation studies*

To investigate the selectivity of the extractants, a solution was made containing base-soluble elements reported to occur in leachates obtained from irradiaded $UAl_x$ targets in concentrations of approximately 1000 ppm.[10,47,48] These were molybdenum, aluminium, cesium, iodine and tellurium, respectively added as $Na_2MoO_4$, $NaAl(OH)_4$, CsOH, $NaIO_4$ and $Te(OH)_6$. The alkalinity of the feed solution was varied and the extraction of each element was studied. Data on the exact composition and concentration of industrial leach solutions of irradiated $UAl_x$ targets are scarce, as these details are generally not disclosed by producers. There is some

View Article Online
DOI: 10.1039/C9GC01626K

ambiguity in the literature about the presence of Ru and Zr in such leachates. A handful of authors report the partial leaching of Ru and Zr[10] or Ru[26] in such solutions. Other authors explicitly report these elements to be insoluble in the alkaline leachates.[6,48] Their solubility thus appears to depend very strongly on the exact leaching conditions used. Cs and Te are generally reported to be present in acidic leachates, but due to the high solubility of these elements in alkaline solutions, their presence cannot be excluded from alkaline leachates. The compounds as which the elements were added contain each element in its highest stable oxidation state, reflecting their speciation after alkaline oxidative leaching or alkaline leaching followed by oxidation. The concentration of each element in $UAl_x$ target leachates is again highly dependent on the exact leaching process used by the manufacturer, which is often tailored to the ensuing purification process. Therefore, concentrations of 1000 ppm were chosen as this allows accurate quantification while being low enough to prevent saturation of the extractant. Studies reported on by the International Atomic Energy Agency in 1989 reported a realistic total molybdenum concentration after leaching to be roughly 20 000 ppm (32 mg dissolved in 1.575 mL of leach solution).[49] For iodine, this value was 4000 ppm (6.7 mg dissolved in 1.575 mL of leach solution).

The first system to be investigated was undiluted, presaturated $[P_{66614}]_2[SO_4]$. The results of this assay are shown in Fig. 7. The percentages extraction (%E) are shown rather than the distribution ratios, to more clearly illustrate the degree of separation obtained. As the percentage extraction is a function of the phase ratio, it should be noted that a 2:1 aqueous to organic ratio was used in this study. Initial pH-values are shown in Fig. 7, although the pH does not change significantly during the extraction process as the mechanism does not involve proton or hydroxide exchange.

Clearly, neat $[P_{66614}]_2[SO_4]$ exhibits selectivity for molybdenum over the other evaluated elements, especially at higher alkalinity. At 2.00 mol $L^{-1}$ NaOH, 91% of molybdenum is

View Article Online
DOI: 10.1039/C9GC01626K

extracted, with only 6% of the aluminum coextracted. The strong pH-dependence of the extraction of tellurium results from its polyprotic nature. The transition of $H_4TeO_6^{2-}$ to the more strongly charged $H_3TeO_6^{3-}$ has a theoretical $pK_a$ of 14.3.[50] On the grounds of their respective charge densities, only the former is expected to report significantly to the organic phase in exchange for dianionic sulfate.[44] Similar arguments apply to periodate. In alkaline solutions, metaperiodate ($IO_4^-$) hydrolyzes to trianionic orthoperiodate ($H_2IO_6^{3-}$). The theoretical $pK_a$ for the transition of $H_3IO_6^{2-}$ to $H_2IO_6^{3-}$ is 11.6, although the former dimerizes, affecting the equilibrium.[51] As a result of these hydrolyses, the extraction of both iodine and tellurium is observed to decrease strongly from pH 13 to 14.3, down to negligible values.

Extraction of aluminum also decreases markedly towards higher pH values. While Moolenaar and McKeever suggested the formation of $Al_2O(OH)_6^{2-}$ above 1.5 mol $L^{-1}$ NaOH on the basis of vibrational and $^{27}$Al NMR spectra, this form only becomes dominant above 6 mol $L^{-1}$ NaOH. A more plausible reason is the dehydrating effect of concentrated electrolyte solutions on the organic phase. This could even be observed visually during presaturation of the organic phases, as the volume increase of the organic phase was much less significant for samples equilibrated with higher NaOH concentrations. As discussed above, reduced water content in the organic phase increases the differences in solvation experienced by anions in both phases, driving distribution ratios to more extreme values in either direction.

The extraction of cesium was very low at all investigated pH values. Cesium does not significantly form anionic species and thus cannot be extracted *via* a mechanism similar to that proposed in Eq. 4. Note that due to analytical errors of a few percent, some extraction percentages for cesium appear slightly below 0%.

View Article Online
DOI: 10.1039/C9GC01626K

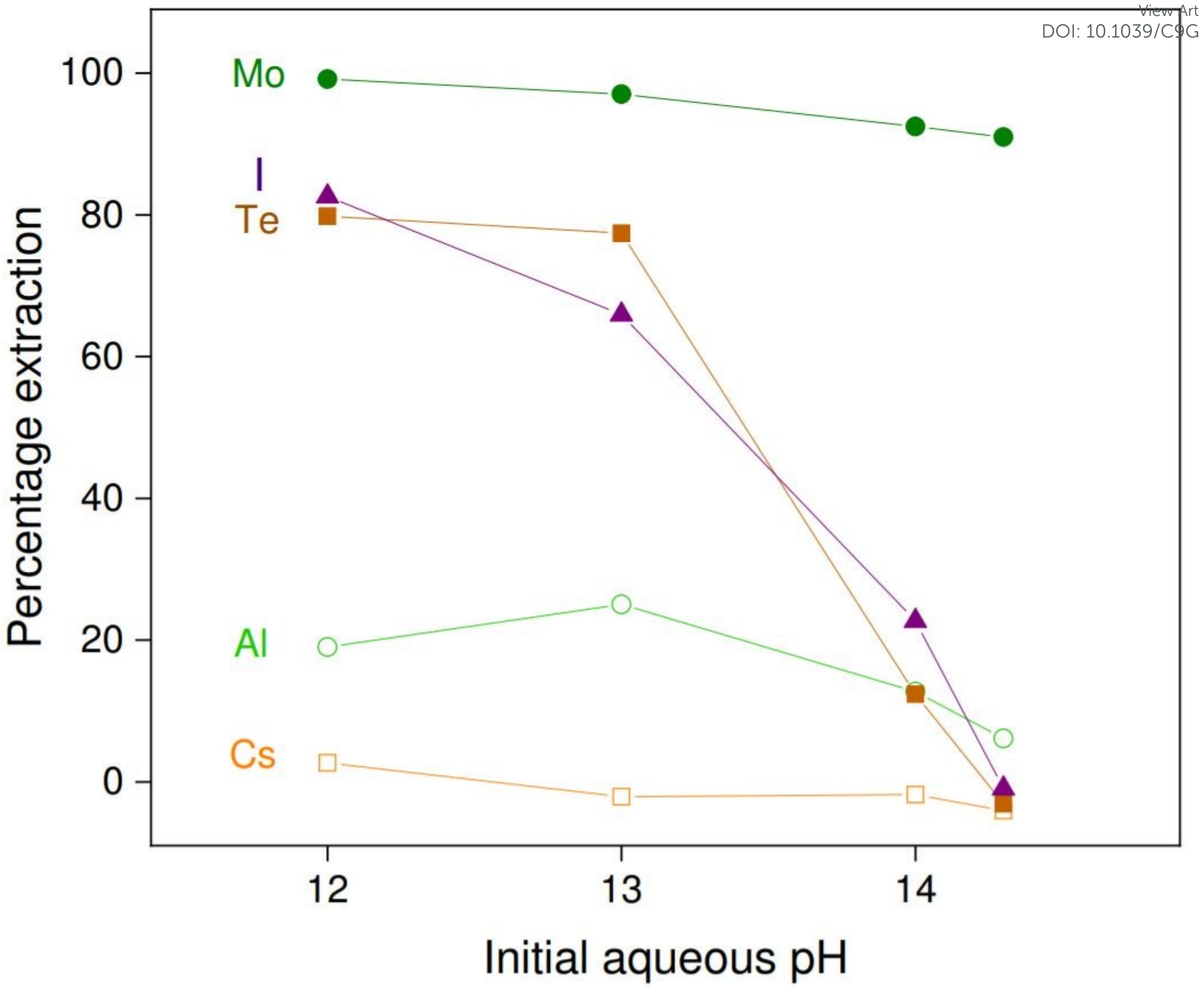


*Fig. 7: Variation of the percentages extraction of Mo (solid circles), Te (solid squares), I (solid triangles), Al (unfilled circles) and Cs (unfilled squares) as a function of the initial aqueous pH. Elements were present in 1000 ppm concentrations as their hydroxides or highest valence sodium salts. The organic phase was undiluted* $[P_{66614}]_2[SO_4]$ *presaturated with water containing an appropriate concentration of NaOH. A phase ratio of 2:1 (aqueous to organic) was used at 30 °C.*

Similar results are obtained for extractions to an organic phase composed of a 1:1 volume mixture of $[P_{66614}]_2[SO_4]$ in 1-octanol, under identical conditions (Fig. 8). The co-extraction of aluminum, iodine and tellurium is suppressed compared to neat $[P_{66614}]_2[SO_4]$, presumably due to the reduced water content of the organic phase, enhancing differences in solvation of the anionic species in both phases and thus resulting in higher selectivity. Note again that some very poorly extracted metals display a %*E* below 0% due to analytical errors.

View Article Online
DOI: 10.1039/C9GC01626K

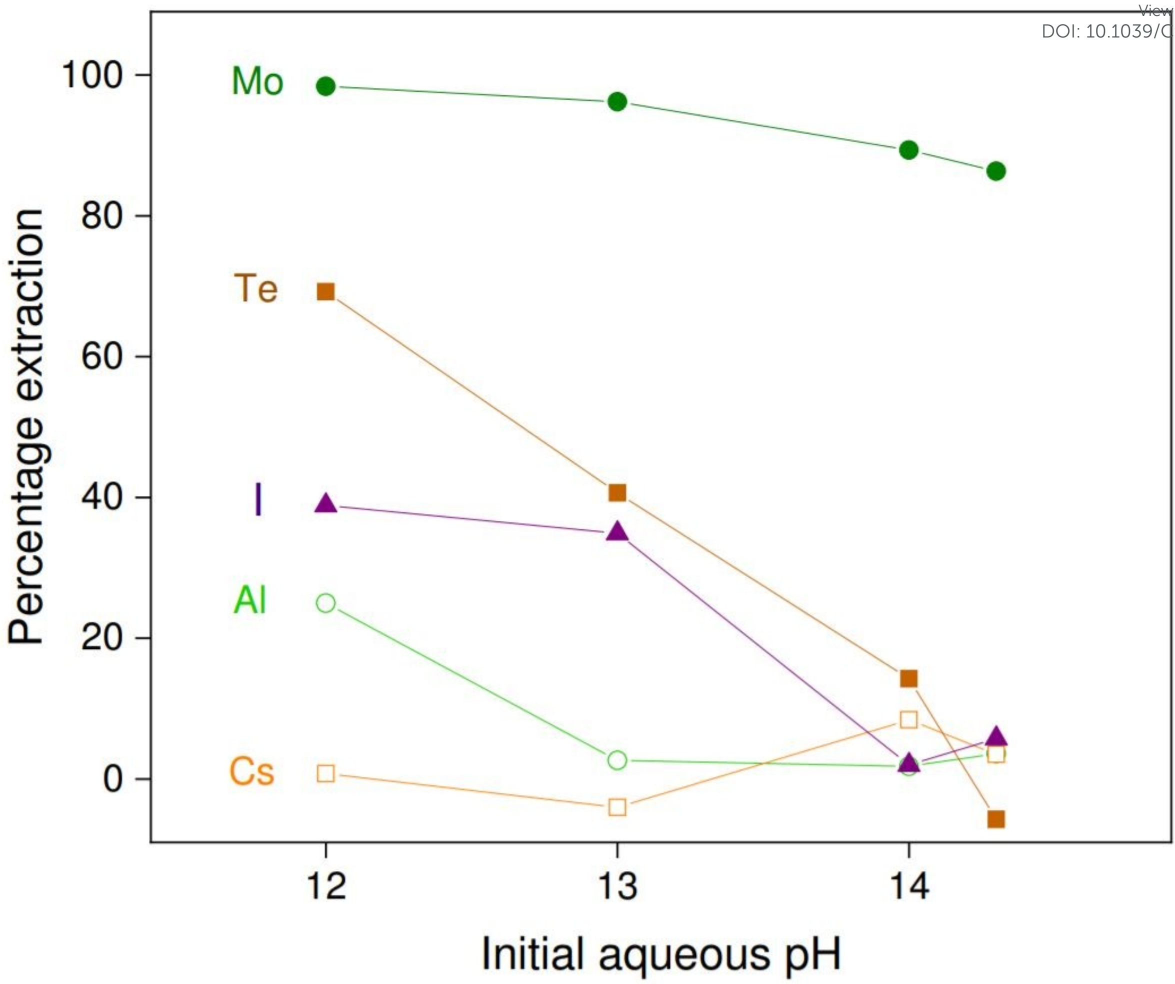


*Fig. 8: Variation of the percentages extraction of Mo (solid circles), Te (solid squares), I (solid triangles), Al (unfilled circles) and Cs (unfilled squares) as a function of the initial aqueous pH. Elements were present in 1000 ppm concentrations as their hydroxides or highest valence sodium salts. The organic phase was 1:1 $[P_{66614}]_2[SO_4]$ in 1-octanol, presaturated with water containing an appropriate concentration of NaOH. A phase ratio of 2:1 (aqueous to organic) was used at 30 °c.*

$[EhEhT_{23}]_2[SO_4]$ is a weaker extractant for Mo than $[P_{66614}]_2[SO_4]$ and is miscible with water at low NaOH concentrations. However, it also displays a very low affinity for tellurium, aluminum and iodine when diluted with 1-octanol. Diluted $[EhEhT_{23}]_2[SO_4]$ is thus suitable as a selective extractant for molybdenum at comparatively low basicities. Based on the extraction results for molybdenum shown in Fig. 6, an extractant concentration of 30 vol% was chosen. The extraction results for mixed feed solutions displayed in Fig. 9 show that the extraction of molybdenum is poor at higher alkalinity. This effect is also seen in the other systems described above, but the impact on the percentages extraction is exacerbated in this system by the lower

View Article Online
DOI: 10.1039/C9GC01626K

distribution ratios for Mo. The suppression of molybdenum extraction is most likely caused by competitive extraction of hydroxide.[52] The lowest degree of coextraction of impurities is obtained at 1.00 mol $L^{-1}$ NaOH. The slight uptick in the degree of coextraction of tellurium and iodine at 2.00 mol $L^{-1}$ NaOH may be a result of a salting-out effect induced by NaOH. Extraction results for 50 vol% $[EhEhT_{23}]_2[SO_4]$ were generally poorer in terms of both the selectivity and distribution ratios obtained for molybdenum. These are shown in the ESI (Fig.S13).

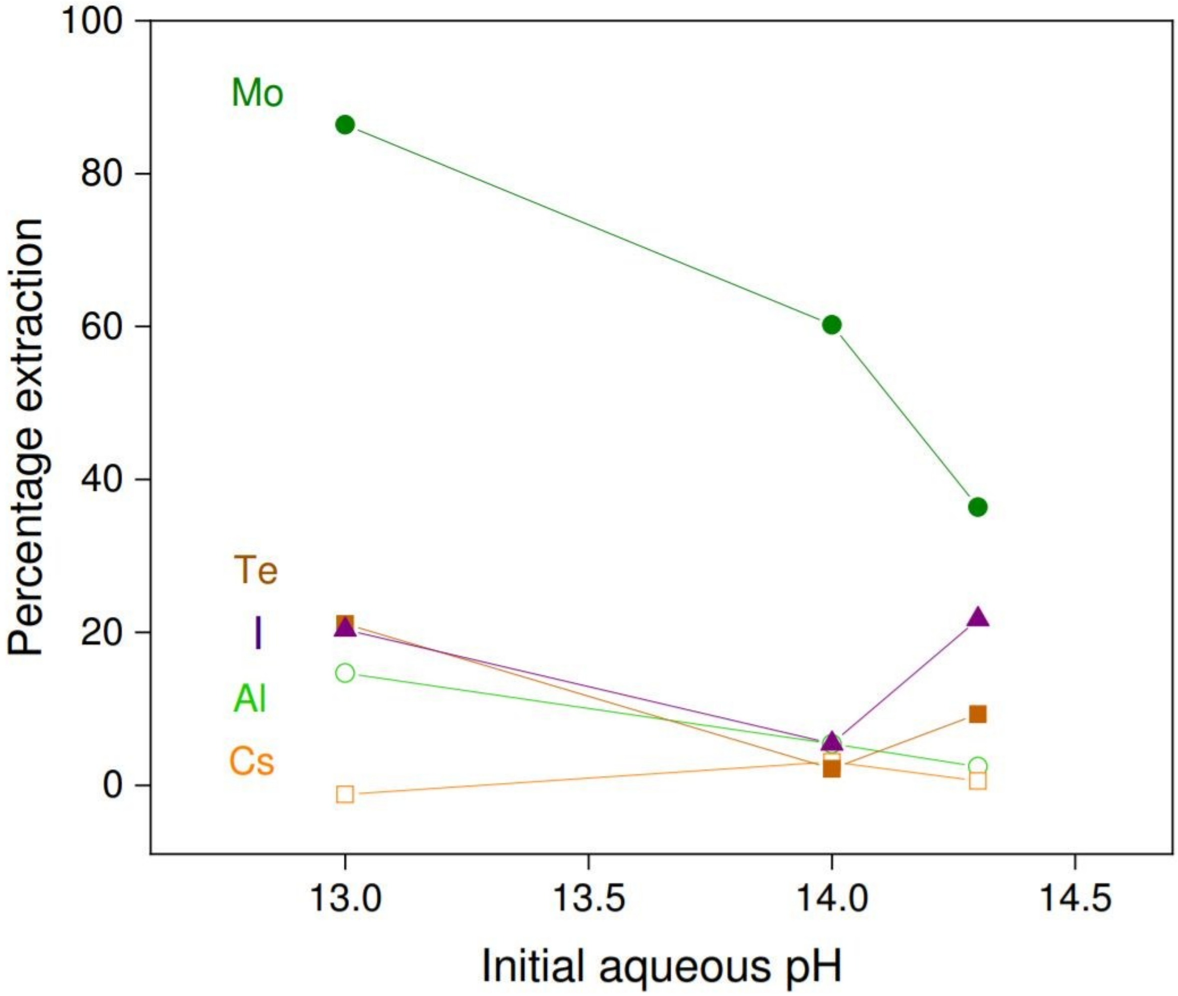


*Fig. 9: Variation of the percentages extraction of Mo (solid circles), Te (solid squares), I (solid triangles), Al (unfilled circles) and Cs (unfilled squares) as a function of the initial aqueous pH. Elements were present in 1000 ppm concentrations as their hydroxides or highest valence sodium salts. The organic phase was 30 vol%* $[EhEhT_{23}]_2[SO_4]$ *diluted in 1-octanol, presaturated with water containing an appropriate concentration of NaOH. A phase ratio of 2:1 (aqueous to organic) was used at 30 °C.*

View Article Online
DOI: 10.1039/C9GC01626K

In the systems described above, conditions exist in which all radiochemically active impurities are left in the aqueous phase, and molybdenum is the only element of the mixture to be significantly extracted. Because of this, the initial feed solution will be the only waste fraction that contains high concentrations of radioisotopes if the process is applied to the isolation of $^{99}$Mo. If a scrubbing step would be included, the aqueous solution used in this step would also contain a limited amount of radioactive isotopes and would have to be treated as radioactively contaminated waste. The total volume of radioactive waste will thus be relatively limited. This contrasts to chromatographic separations, wherein the impurities are eluted over several column bed volumes of salt or acid solutions, resulting in high volumes of radiochemical waste.

*Stripping of molybdenum*

Stripping with concentrated sulfate solutions was inefficient, in spite of the expected reversal of the extraction equilibrium at high sulfate activity. Presumably, the high concentration of cosmotropic (strongly hydrated) sulfate salts in the aqueous phase results in the salting out of molybdate, causing the equilibrium constant of the reaction described by Eq. 4 to increase. Results of stripping experiments with sulfate salts can be found in the ESI (Table S1).

Effective stripping was achieved by contacting the loaded organic phase with a 1.00 mol L$^{-1}$ solution of sodium hydrogen carbonate. As a result, $MoO_4^{2-}$ and $SO_4^{2-}$ are displaced by $HCO_3^-$ in the organic phase. The high pH of the stripping liquor prevents the formation of protonated molybdates or polyoxomolybdates, which are less strongly hydrated and more difficult to strip.

Prior to stripping, the organic phases were saturated with 2.00 mol L$^{-1}$ NaOH and loaded from a solution of 2.00 mol L$^{-1}$ NaOH containing 1000 ppm Mo as $Na_2MoO_4$ in a 2:1 aqueous-to-organic phase volume ratio. A 4:1 aqueous-to-organic phase volume ratio upon stripping ensured recovery of approximately 90% of all molybdenum from a 1:1 volume mixture $[P_{66614}]_2[SO_4]$ in 1-octanol and 30 vol% $[EhEhT_{23}]_2[SO_4]$ in 1-octanol. Stripping of

View Article Online
DOI: 10.1039/C9GC01626K

molybdenum from neat $[P_{66614}]_2[SO_4]$ was poorer at about 50%. A cumulative stripping percentage of 89% could be achieved after a second stripping cycle. This second contact was more effective than the first, in the sense that the distribution ratio of Mo was much lower. This can be attributed to the higher equilibrium concentration of $HCO_3^-$ in the aqueous phase, as it is no longer consumed by the displacement of sulfate anions from the organic phase.

Table 2: Stripping of molybdenum from loaded[a] organic phases using 1.00 mol $L^{-1}$ $NaHCO_3$ in a 4:1 aqueous-to-organic phase volume ratio.

| | %S | D |
|---|---|---|
| $[P_{66614}]_2[SO_4]$ in 1-octanol (1:1) | 88 | 0.52 |
| $[EhEhT_{23}]_2[SO_4]$ in 1-octanol (30 vol%) | 89 | 0.49 |
| $[P_{66614}]_2[SO_4]$ undiluted | 56 | 4.47 |
| $[P_{66614}]_2[SO_4]$ undiluted, second contact | 89[b] | 1.39 |

[a] Loading conditions: aq:org = 2, 1000 ppm Mo as $Na_2MoO_4$, 2.00 mol $L^{-1}$ NaOH.
[b] Cumulative stripping percentage.

Upon stripping, the sulfate extractant is converted to its hydrogen carbonate analog due to the exchange of sulfate anions for hydrogen carbonate anions. This conversion is evidenced by the disappearance of the sulfate asymmetric S-O stretching band in the infrared spectrum, as well as the appearance of additional bands centered around 1614 and 1381 $cm^{-1}$. These signals are attributed to the bicarbonate asymmetric and symmetric stretching modes, respectively.[53] To reverse this conversion and regenerate the extractant for reuse, the organic phase after stripping is contacted with an alkaline sulfate solution, containing NaOH (2.00 mol $L^{-1}$) and $Li_2SO_4$ (1.00 mol $L^{-1}$). An aqueous-to-organic phase volume ratio of 2:1 is used. The basicity of the aqueous solution results in the deprotonation of the hydrogen carbonate anions in the organic phase, which then become more strongly hydrated and are thus easily displaced by the sulfate anions in the aqueous phase. The reaction is further driven by the precipitation of $Li_2CO_3$. The infrared

View Article Online
DOI: 10.1039/C9GC01626K

spectra displayed in Fig. 10 show the evolution of the sulfate S–O stretching band and the bicarbonate C–O stretching bands during various stages of the stripping and regeneration process. Contacting the organic phase once with the alkaline sulfate solution was sufficient to regenerate the extractant to its sulfate form, as evidenced by the overlapping profiles of the infrared spectra before stripping and after regeneration.

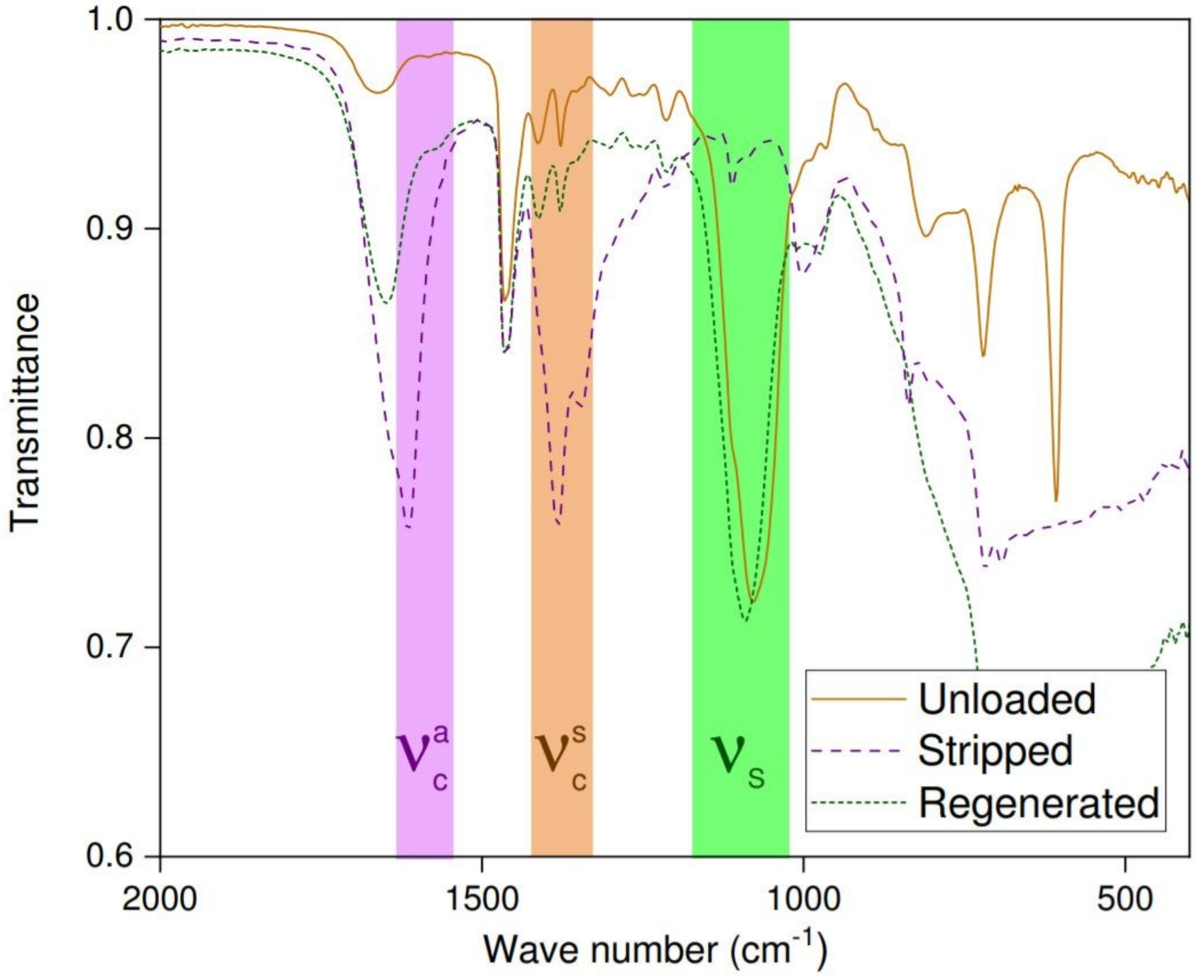


*Fig. 10: Comparison of the infrared spectra of neat $[P_{66614}]_2[SO_4]$ before loading, after stripping and after regeneration. The sulfate asymmetrical stretching band is highlighted and labeled as $\nu_S$. The bicarbonate symmetrical and asymmetrical stretching bands are labeled as $\nu^s_C$ and $\nu^a_C$, respectively. Spectra were normalized by equalizing the transmittance of the C-H stretch bands for a more accurate comparison of the intensity of the sulfate stretching bands.*

View Article Online
DOI: 10.1039/C9GC01626K

### *Estimate of radiochemical waste production*

High levels of confidentiality surround the details of current production methods for radiopharmaceutical $^{99}$Mo. Hence, it is difficult to determine exactly to which degree the production of radiochemical waste can be reduced by switching from a chromatography to a solvent extraction-based purification. Moreover, the exact values will depend on the nature of the leaching procedure and the pretreatment applied to the leachate. However, the Mallinckrodt/ECN has disclosed per-Curie volumes of intermediate and low-level waste generated in the $^{99}$Mo production process. The Mallinckrodt/ECN process also entails direct processing of an alkaline leachate of irradiated targets, without acidification. In total, roughly 22.0 L of intermediate-level liquid waste and 19.6 L of low-level liquid waste is produced per 3000 Ci of molybdenum-99. Furthermore, many radionuclides remain adsorbed to the column materials, implying that these must also be treated as solid radiochemical waste.[6] An estimate of the volume of radiochemical waste produced by the solvent extraction process can be obtained using literature data available for the IRE process. The International Atomic Energy Agency reported in 1989 that Belgium's IRE requires 1.575 mL of 3 mol L$^{-1}$ NaOH to dissolve three irradiated UAl$_x$ targets. According to Ponsard, this amount of target material amounts to 3000 Ci of $^{99}$Mo after irradiation, or 2325 Ci of $^{99}$Mo after irradiation and cooling.[54] Dilution to 2 mol L$^{-1}$ NaOH, the hydroxide concentration used in this study, yields roughly 2.40 mL of leachate, ready for solvent extraction. In addition to the raffinate, the solvent extraction procedure also generates 1-3 equal volumes of scrubbing and stripping solutions (depending on the applied number of scrubbing stripping steps), a final waste volume of about 10 mL per 2325 Ci of $^{99}$Mo is obtained.

View Article Online
DOI: 10.1039/C9GC01626K

*Comparison to existing molybdenum extraction systems*

Most extraction systems for the separation molybdate from other oxometalates are optimized to work from acidic solutions.[57] However, as mentioned above, acidic leaching offers poor selectivity for molybdenum and brings uranium and many unwanted fission products into solution, in particular the lanthanides.[6,47] Imam and El-Nadi reported on the extraction of molybdenum from NaOH solutions by diluted methyltrioctylammonium hydroxide.[52] The mechanism by which molybdenum is extracted closely resembles that found for the sulfate systems in this work. In the hydroxide system, hydroxide ions from the organic phase are exchanged for aqueous molybdate anions in a 2:1 ratio. In spite of the mechanistic similarities, this system would be troublesome if applied to $UAl_x$ leachates. Anion-exchange processes are only selective for molybdate over periodate and tellurate at very high NaOH concentrations (>1 mol $L^{-1}$) due to the hydrolysis of the latter two species, as reported above. However, these conditions are used to strip molybdate from the hydroxide ionic liquid in the work of Imam and El-Nadi. It would thus be impossible to obtain both effective and selective extraction of molybdenum over iodine and tellurium. Furthermore, ammonium salts such as the one used as extractant in this reference generally exhibit very poor resistance to alkaline conditions due to the occurrence of the Hoffman elimination, especially at the elevated temperatures pertinent in radioactive solutions.[30,55,56] Finally, to extract 90% of the molybdenum from the feed solution using this system, the NaOH concentration must be lowered to 0.1 M, requiring a 30-fold dilution of the leachate. By contrast, our sulfate-based systems efficiently extract molybdenum even from 1–2 mol $L^{-1}$ NaOH feed solutions.

## Conclusion

Two new basic sulfate extractants were synthesized and characterized. These compounds are liquids at ambient temperatures and can thus be considered ionic liquids. These extractants

View Article Online
DOI: 10.1039/C9GC01626K

display good selectivity for molybdenum over other elements present in alkaline leachates of irradiated $UAl_x$ alloy targets at highly alkaline and oxidative conditions. The triazolium extractant exhibits the highest resistance towards decomposition induced by alkali, but is a weaker extractant than its phosphonium counterpart. The phosphonium extractant exhibits very high affinity for molybdate and can be used without diluent, *i.e.* as an ionic liquid. Stripping can be accomplished by contacting the loaded organic phase with sodium hydrogen carbonate solution. The extractant is finally regenerated by a single contact with an alkaline sulfate solution. Overall, the phosphonium extractant diluted in 1-octanol displays the best extraction and stripping performance, while the triazolium extractant diluted in 1-octanol exhibits the best long-term reusability. Conditions exist in which these extractants extract only molybdenum and leave other radiochemical impurities in the original feed solution, resulting in a limited volume of radiochemical waste. Therefore, these extractants can be considered as promising alternatives to state-of-the-art methods to purify radiomolybdenum, which rely on chromatography and produce large quantities of radiochemically contaminated waste.

## Supporting Information

View Article Online
DOI: 10.1039/C9GC01626K

Electronic supplementary information (ESI) is available: synthesis and characterization of extractants, $^{1}H$, $^{13}C$ and $^{31}P$ NMR spectra, FT-IR spectra, supplementary extraction and stripping data, determination of phase volume changes upon stripping.

## Conflict of interest

There are no conflicts to declare.

## Acknowledgements

This work was funded by FWO-Flanders (doctoral fellowship to SR). The authors thank Sofia Riaño, Karen Van Hecke and Michiel Van de Voorde for fruitful discussions and useful suggestions. The authors also wish to thank Bieke Onghena for sharing unpublished results on the synthesis of sulfate ionic liquids. The authors further acknowledge Karel Duerinckx for NMR spectroscopy.

## References

View Article Online
DOI: 10.1039/C9GC01626K

1 P. Verbeek, *Report on Molybdenum 99 Production for Nuclear Medicine 2010-2020,* OECD Nuclear Energy Agency, Boulogne-Billancourt, 2008.

2 J. R. Dilworth and S. J. Parrott, *Chem. Soc. Rev.*, 1998, **27**, 43–55.

3 M. D. Bartholomä, A. S. Louie, J. F. Valliant and J. Zubieta, *Chem. Rev.*, 2010, **110**, 2903–2920.

4 M. C. Lagunas-Solar, P. M. Kiefer, O. F. Carvacho, C. A. Lagunas and Y. P. Cha, *Int. J. Rad. Appl. Instrum. A*, 1991, **42**, 643–657.

5 S. C. van der Marck, A. J. Koning and K. E. Charlton, *Eur. J. Nucl. Med. Mol. Imaging*, 2010, **37**, 1817–1820.

6 *Management of radioactive waste from $^{99}$Mo production,* IAEA, Vienna, 1998.

7 S.-K. Lee, G. J. Beyer and J. S. Lee, *Nucl. Eng. Technol.*, 2016, **48**, 613–623.

8 O. Y. Kochnov, V. V. Pozdeev, A. I. Krasheninnikov and N. V. Zakharov, *Radiochemistry*, 2012, **54**, 188–192.

9 H. Arino, A. Thornton, H. Kramer and J. Mc Govern, US Pat. 3 799 883 A, 1974.

10 A. Rao, A. Kumar Sharma, P. Kumar, M. M. Charyulu, B. S. Tomar and K. L. Ramakumar, *Appl. Radiat. Isot.*, 2014, **89**, 186–191.

11 H. Arino and H. H. Kramer, *Int. J. Appl. Radiat. Isot.*, 1978, **29**, 97–102.

12 D. Wu, S. Landsberger and B. Buchholz, *Processing of LEU targets for $^{99}$Mo production--testing and modification of the Cintichem process*, Argonne National Laboratory, Lemont, 1995.

View Article Online
DOI: 10.1039/C9GC01626K

13 D. S. Hwang, W. M. Choung, Y. K. Kim, J. H. Park and S. J. Park, *J. Radioanal. Nucl. Chem.*, 2002, **254**, 255–262.

14 W. L. Cheng, C. S. Lee, C. C. Chen, Y. M. Wang and G. Ting, *Int. J. Rad. Appl. Instrum. A*, 1989, **40**, 315–324.

15 M. Yamaura, A. A. Freitas, A. P. G. Yamamura, R. M. N. Tanaka, C. A. L. G. de O. Forbicini, R. L. Camilo and I. C. Aurajo, in *RETR 2010 - 32nd Interantional Meeting on Reduced Enrichment for Research and Test Reactors*, Lisbon, Portugal, 2010.

16 K. Dadachova, K. La Riviere and P. Anderson, *J. Radioanal. Nucl. Chem.*, 1999, **240**, 935–938.

17 R. K. Barnes and R. E. Boyd, *Int. J. Appl. Radiat. Isot.*, 1982, **33**, 479–481.

18 M. A. El-Absy, *Radiochim. Acta*, 1991, **55**, 23–28.

19 G. E. Dale, D. A. Dalmas, M. J. Gallegos, K. R. Jackman, C. T. Kelsey, I. May, S. D. Reilly and G. M. Stange, *Ind. Eng. Chem. Res.*, 2012, **51**, 13319–13322.

20 K. Motojima and M. Tanase, *Int. J. Appl. Radiat. Isot.*, 1977, **28**, 485–489.

21 R. Münze, O. Hladik, G. Bernhard, W. Boessert and R. Schwarzbach, *Int. J. Appl. Radiat. Isot.*, 1984, **35**, 749–754.

22 R. B. Manolkar, S. P. Hasilkar and A. V. Jadhav, *J. Radioanal. Nucl. Chem.*, 2002, **251**, 273–276.

23 S. Hasilkar, R. Manolkar and A. Jadhav, *J. Radioanal. Nucl. Chem.*, 2002, **251**, 277–280.

24 *Manual for Reactor Produced Radioisotopes*, IAEA, Vienna, 2003.

View Article Online
DOI: 10.1039/C9GC01626K

25 S. Meca, V. Marti, P. J. de, J. Giménez and I. Casas, *Radiochim. Acta*, 2008, **96**, 535–539.

26 C. Conner, S. Aase, D. G. Wygmans, G. F. Vandegrift, D. Wu and S. Landsberger, *Dissolution of low-enriched UO2/Al dispersion plates in alkaline peroxide solution*, Abstracts and papers of the 1997 International RERTR Meeting, Vienna, 1997.

27 M. A. A. Al-Janabi, H. A. Kaleefa, M. G. Jalhoom, E. H. Abbas and A. S. Al-Warith, *J. Radioanal. Nucl. Chem.*, 1987, **111**, 165–175.

28 M. Iqbal and M. Ejaz, *J. Radioanal. Chem.*, 1978, **47**, 25–28.

29 A. G. C. Nair, S. K. Das, S. M. Deshmukh and S. Prakash, *Radiochim. Acta*, 1992, **57**, 29–32.

30 S. Sowmiah, V. Srinivasadesikan, M.-C. Tseng and Y.-H. Chu, *Molecules*, 2009, **14**, 3780–3813.

31 D. Landini, A. Maia and A. Rampoldi, *J. Org. Chem.*, 1986, **51**, 3187–3191.

32 K. C. Lethesh, W. Dehaen and K. Binnemans, *RSC Adv.*, 2013, **4**, 4472–4477.

33 B. Siegel, *J. Am. Chem. Soc.*, 1979, **101**, 2265–2268.

34 C. Maton, N. D. Vos, B. I. Roman, E. Vanecht, N. R. Brooks, K. Binnemans, S. Schaltin, J. Fransaer and C. V. Stevens, *ChemPhysChem*, 2012, **13**, 3146–3157.

35 K. M. Hugar, H. A. Kostalik and G. W. Coates, *J. Am. Chem. Soc.*, 2015, **137**, 8730–8737.

36 C. Deferm, M. Van de Voorde, J. Luyten, H. Oosterhof, J. Fransaer and K. Binnemans, *Green Chem.*, 2016, **18**, 4116–4127.

37 T. Welton, *Chem. Rev*, 1999, **99**, 2071-2084.

View Article Online
DOI: 10.1039/C9GC01626K

38 J. S. Wilkes, *Green Chem.*, 2002, **4**, 73–80.

39 S. Raiguel, J. Thomas, K. Binnemans and W. Dehaen, *Eur. J. Org. Chem.*, 2018, **2018**, 4850-4856.

40 C. M. Alder, J. D. Hayler, R. K. Henderson, A. M. Redman, L. Shukla, L. E. Shuster and H. F. Sneddon, *Green Chem.*, 2016, **18**, 3879–3890.

41 D. B. Parry, M. G. Samant, H. Seki, M. R. Philpott and K. Ashley, *Langmuir*, 1993, **9**, 1878–1887.

42 T. Wende, N. Heine, T. I. Yacovitch, K. R. Asmis, D. M. Neumark and L. Jiang, *Phys. Chem. Chem. Phys.*, 2016, **18**, 267–277.

43 S. S. Saleem and G. Aruldhas, *J. Solid State Chem.*, 1982, **42**, 158–162.

44 D. Dupont, D. Depuydt and K. Binnemans, *J. Phys. Chem. B*, 2015, **119**, 6747–6757.

45 J. Zhou, G. Santambrogio, M. Brümmer, D. T. Moore, L. Wöste, G. Meijer, D. M. Neumark and K. R. Asmis, *J. Chem. Phys.*, 2006, **125**, 111102.

46 C. Reichardt and T. Welton, in *Solvents and Solvent Effects in Organic Chemistry*, Wiley-Blackwell, 2010, pp. 359–424.

47 G. E. Androne and A. Matei, *Experiments for separation and purification of Mo-99 from uranium solution with fission products as tracers*, Romanian Authority for Nuclear Activity- Institute of Nuclear Research România, Pitesti-Mioveni, 2007

48 T. N. van der Walt and P. P. Coetzee, *Radiochim. Acta*, 2009, **92**, 251–257.

49 *Fission Molybdenum For Medical Use*, Proceedings of a Technical Committee Meeting Organized by the International Atomic Energy Agency, IAEA, Vienna, 1989.

View Article Online
DOI: 10.1039/C9GC01626K

50 G. K. Schweitzer and L. L. Pesterfield, *The Aqueous Chemistry of the Elements*, Oxford University Press, 2010.

51 J.-L. Burgot, *Ionic Equilibria in Analytical Chemistry*, Springer Science & Business Media, 2012.

52 D. M. Imam and Y. A. El-Nadi, *Hydrometallurgy*, 2018, **180**, 172–179.

53 D. L. Bernitt, K. O. Hartman and I. C. Hisatsune, *J. Chem. Phys.*, 1965, **42**, 3553–3558.

54 B. Ponsard in *2015 Topical Meeting on Molybdenum-99 Technological Development*, National Nuclear Security Administration, 2015.

55 M. Hayyan, F. S. Mjalli, M. A. Hashim, I. M. AlNashef and T. X. Mei, *J. Ind. Eng. Chem.*, 2013, **19**, 106–112.

56 Q. Zhang, Q. Wang, S. Zhang, X. Lu and X. Zhang, *ChemPhysChem*, 2016, **17**, 335–351.

57 T. H. Nguyen and M. S. Lee, *Geosystem Eng.*, 2016, **19**, 247–259.