



Synthesis and Application of Tricaprylmethyl ammoniumthiosalicylate as Extracting Agent for Actinide Ions[†]

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Tricaprylmethylammonium thiosalicylate ([A336][TS]), a thiol-containing task specific ionic liquid was prepared using Aliquat 336[®] and thiosalicylic acid. The structure of the synthesized final product ([A336][TS]) was confirmed by ¹H NMR, FTIR and HPLC/ESI-MS/MS. In the extraction of uranium and neptunium from a nitric acid solution with [A336][TS] ionic liquid, distribution coefficients (D) of uranium and neptunium increased as the nitric acid concentration increased.

Keywords: Tricaprylmethylammonium thiosalicylate, HPLC/ESI-MS/MS, Uranium, Neptunium, Extraction.

INTRODUCTION

Owing to their unique chemical and physical properties, ionic liquids (ILs) has become one of the most interesting and rapidly developing areas of modern physical chemistry, technologies and engineering, including constructing new devices for various applications. In the nuclear chemistry field, applications of ionic liquids act as media for the reprocessing of spent nuclear fuels. If ionic liquids are applied to the reprocessing processes as alternative media to the conventional extracting agents consisting of volatile organic compounds, the processes are expected to become safer because of their properties. Nuclear fuel cycle radioactive waste treatment has also been expected, for example, the technologies for radioactive liquid waste treatment from the nuclear fuel cycle, separation technologies of a nuclide in nuclear liquid waste and treatment technologies of a nuclear waste from pyroprocessing of spent fuel. Further development of this field depends on R&D in ionic liquids chemistry and revealing new perspective practical approaches¹⁻³. The use of hydrophobic chelating agent and/or the design of task specific ionic liquid (TSIL) by the introduction of chelating functions on the organic ion can greatly increase the metal affinity for the ionic liquid phase providing an extraction yield much greater than those found with conventional molecular solvents. Ionic liquids with a strong coordinating anion represent another strategy to enhance the affinity of a metal for the ionic liquid phase⁴.

The synthesis of task specific ionic liquids (TSILs), their characterization and possible applications have been developing progressively, as the properties of this class of organic salts with melting points below the boiling point of water have gained intensive attention in nearly all fields of chemistry⁵. Task specific ionic liquids were widely used for the selective liquid/liquid extraction of heavy metals from aqueous systems and the results have been reported by many researchers⁵⁻¹⁰. In contrast, the newly synthesized ionic liquids described here are based on a hydrophobic, long chain tetraalkylammonium cation with aliphatic and aromatic carboxylate anions. Furthermore, tricaprylmethylammonium thiosalicylate [A336][TS], possesses a thiol-containing anion. Task specific ionic liquids have received recent attention for application of environmental friendly technologies for nuclear fuel cycle waste treatment.

In this study, we synthesized [A336][TS], a thiol-containing task specific ionic liquid using Aliquat 336[®] and thiosalicylic acid and characterized by ¹H NMR, FTIR and ESI-MS measurements. The possible use as an extracting agent for the extraction of actinide ions from nitric acid solution is also studied.

EXPERIMENTAL

Synthesis of [A336][TS] task-specific ionic liquid: Tricaprylmethylammonium thiosalicylate ([A336][TS]), a thiol-containing task specific ionic liquid was prepared by stirring equimolecular amounts of Aliquat 336[®] as cationic

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precursor and thiosalicylic acid as a Brønsted acid in a sodium hydroxide solution (Fig. 1). The structure of the synthesized final product of [A336][TS] was confirmed by ^1H NMR, FTIR and HPLC/ESI-MS/MS analyses.

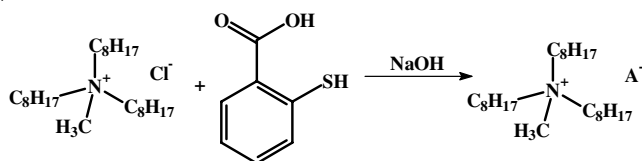


Fig. 1. Synthesis of tricaprylmethylammonium thiosalicylate [A336][TS], a thiol-containing task specific ionic liquid

Extraction of uranium and neptunium: All reagents used in this work were of chemical reagents grade and used as received. Neptunium obtained from AEA Technology in England as ^{237}Np dissolved in 2 M HNO_3 was used without further purification. Uranium was used as UO_2^{2+} resulting from dissolving $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich Co.) in nitric acid. Batch extractions of uranium and neptunium were carried out by mixing vigorously [A336][TS] ionic liquid and the aqueous nitric acid solution in a 15 mL polypropylene conical tube at $25 \pm 0.5^\circ\text{C}$ for 1 h with a wrist action shaker. The concentration of uranium was determined using a spectrophotometric method with Arsenazo-III agent in a KCl-HCl buffer solution at 652 nm. In aqueous and organic phases Np was analyzed by a γ -spectrometer with an HP-Ge detector (Oxford Inc., Model 5000 Radiation Multichannel Analyzer).

RESULTS AND DISCUSSION

Figs. 2 and 3 show the ^1H NMR spectrum and high performance liquid chromatography-electrospray tandem mass spectrometry (HPLC/ESI-MS/MS) analysis results of [A336][TS], respectively. In Fig. 2, chemical shifts between 6.7 and 7.9 ppm can be assigned to aromatic hydrogen atoms of the [TS] (thiosalicylic anion) and chemical shifts between 0.8 and 3.4 ppm could be assigned to hydrogen atoms of [A336] (tricaprylmethylammonium). Fig. 3 shows the thiosalicylic acid component separation in the task specific ionic liquid product ([A336][TS]) by liquid chromatography. We can confirm the same peak at 0.7 min in [A336][TS] and [TS] compounds. Fig. 4 obtained from the HPLC/ESI-MS/MS analysis of [A336][TS] and the single peak at $m/z = 153$ could be assigned to thiosalicylate. The analysis results of Fourier transform infrared spectroscopy (FTIR) spectra of Aliquat 336([A336]), thiosalicylic acid ([TS]) and task specific ionic liquid product [A336][TS] are shown in Fig. 5. Interestingly, an expected absorption band of the thiol group near 2500 cm^{-1} could not be observed for the final product of [A336][TS]. This may be attributable to the generally considered low intensity of this band².

Effect of nitric acid on uranium and neptunium extraction: The distribution coefficient (D_u) value obtained with [A336][TS] in 8 M HNO_3 was 1.38 and that in 2 M HNO_3 was only 0.01. The distribution coefficient (D_u) values obtained with [A336][TS] in a HNO_3 solution for the extraction of uranium from nitric acid solution are 0.01 (at 2 M HNO_3), 0.33 (at 4 M HNO_3), 0.51 (at 6 M HNO_3) and 1.38 (at 8 M HNO_3). The distribution coefficient of uranium was increased with

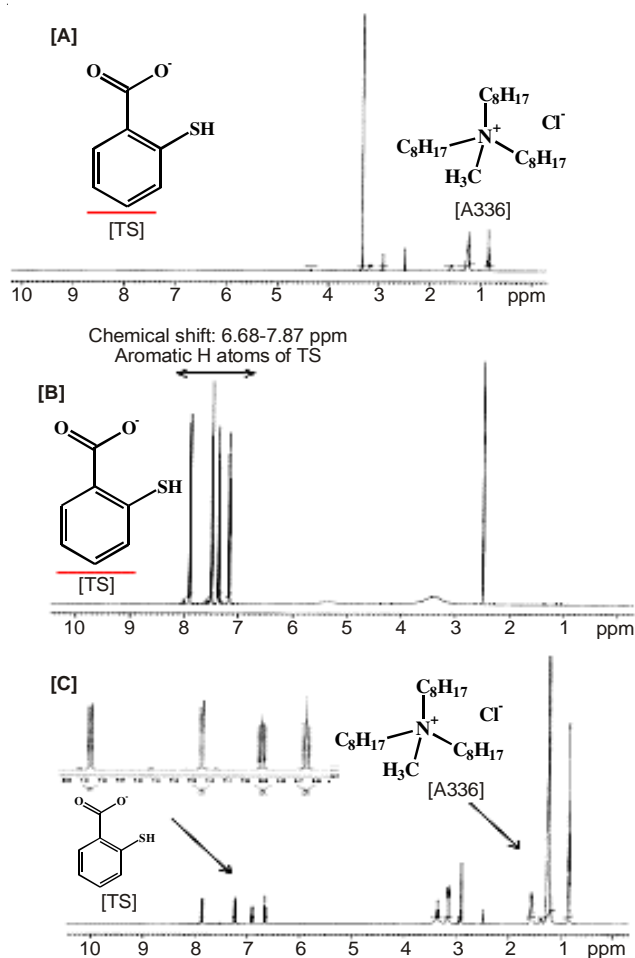


Fig. 2. ^1H NMR spectra of [A] ([A336]), [B] ([TS]) and [C] ([A336][TS])

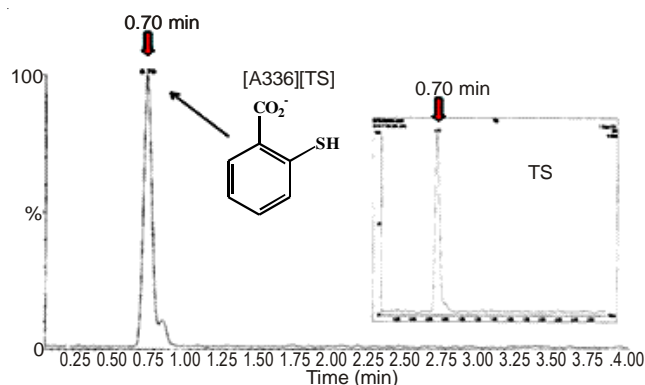


Fig. 3. Thiosalicylate acid component separation in task specific ionic liquid product ([A336][TS]) by LC

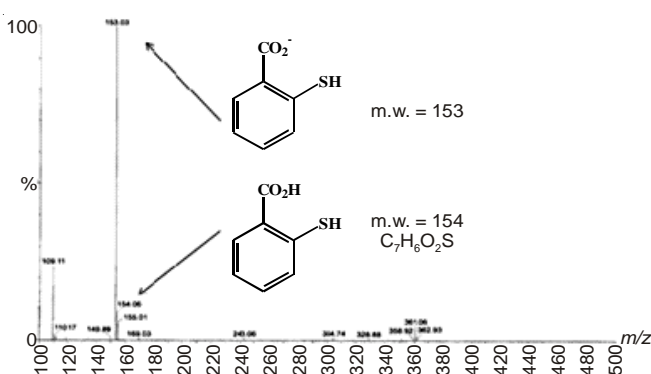


Fig. 4. HPLC/ESI-MS/MS analysis of [A336][TS]

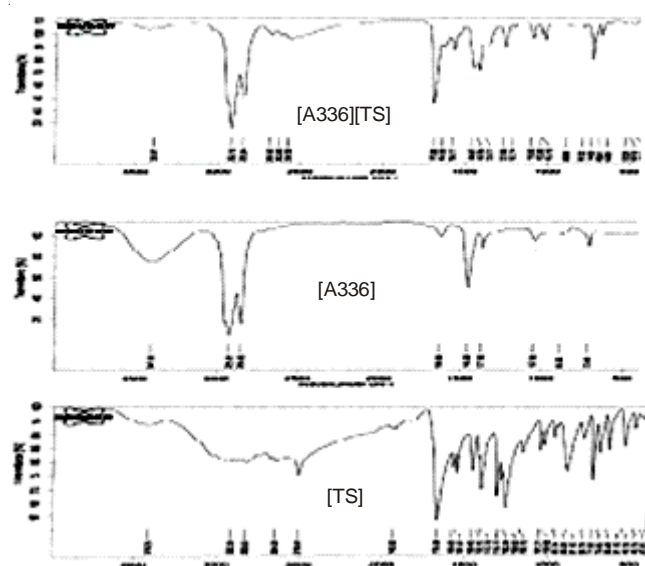


Fig. 5. FTIR spectra of Aliquat 336 ([A336]), thiosalicylic acid ([TS]) and task specific ionic liquid product ([A336][TS])

an increase in the concentration of nitric acid. In Fig. 6, the D_{Np} value obtained with [A336][TS] in the HNO_3 solution for the extraction of neptunium is also increasing as the nitric acid concentration increase. Neptunium(V) ion is stable in the nitric acid solution, but $Np(V)$ ion will change the oxidation state to more extractable ions of $Np(IV)$ and $Np(VI)$ by a disproportionation reaction $[2Np(V) \rightarrow Np(IV) + Np(VI)]$.

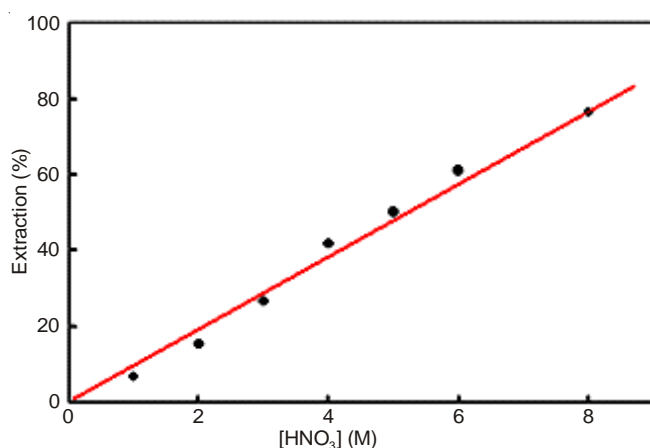


Fig. 6. Extraction of neptunium in nitric acid solution with [A336][TS]

Conclusion

Tricaprylmethylammonium thiosalicylate ([A336][TS]), a thiol-containing task specific ionic liquid was synthesized using Aliquat 336[®] and thiosalicylic acid and final product ([A336][TS]) confirmed by ¹H NMR, FTIR and ESI-MS measurements. Task specific ionic liquid, [A336][TS] was evaluated as a potential extracting agent for uranium and neptunium from a nitric acid solution. The distribution coefficients of uranium and neptunium were increasing as the nitric acid concentration increased. In conclusion, it was seen that task-specific liquid ion, [A336][TS], has a possible use as an extracting agent for the extraction of uranium and neptunium in nitric acid solution.

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