論文 / 著書情報
Article / Book Information

題目(和文)	TPEN類似構造を有する新規疎水性イオン液体による三価ランタニドの抽出と配位に関する研究：ソフトN, ハードO-ハイブリッドドナー戦略
Title(English)	Extraction and coordination performances of trivalent lanthanides by a novel hydrophobic ionic liquid including TPEN analogue structure: A soft N and hard O donor combined strategy
著者(和文)	WuHao
Author(English)	HAO WU
出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第11313号, 授与年月日:2019年9月20日, 学位の種別:課程博士, 審査員:竹下 健二,大貫 敏彦,加藤 之貴,鷹尾 康一朗,塚原 剛彦
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第11313号, Conferred date:2019/9/20, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	融合理工学系 原子核工学コース	系 コース	
学生氏名： Student's Name	Wu Hao		

申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of （ 工学 ）
指導教員（主）： Academic Supervisor(main)	竹下 健二
指導教員（副）： Academic Supervisor(sub)	

要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Lanthanide (Ln) elements play an important role in many fields. Ln^{3+} ions are dominant species in solution and the solid state in most systems. Owing to their similar coordination numbers, chemical properties and ionic radii, the separation of Ln^{3+} from aqueous phase has been identified as one of the biggest technology challenges. With an objective of separation trivalent lanthanides in nitric acid solution. A novel hydrophobic ionic liquid including TPEN analogue structure ($(IL\text{-}TPTNA)^+NTf_2^-$) which also combined one hard O donor and four soft N donor, was designed, synthesized, and characterized. The whole thesis was carefully summarized as the following three aspects:

1. A task specific ionic liquid including *N,N,N',N'*-tetrakis(2-pyridylmethyl)-1,3-propanediamine-2-amide structure ($(IL\text{-}TPTNA)^+NTf_2^-$) was synthesized and its extraction performance of trivalent lanthanides was investigated in nitric acid solution. The extraction kinetic of Eu^{3+} were relatively fast, and extraction equilibrium can be attained within 1 hour at initial pH= 3. The effect of pH values in the aqueous phase indicated that the extraction performance of $(IL\text{-}TPTNA)^+NTf_2^-$ decreased drastically due to the protonation of pyridine groups in highly acidic condition. Complete stripping of Eu^{3+} from ionic liquid phase was possible at 1.0 M HNO_3 solution without the need of using a complex-forming agent in the aqueous phase. With varying the concentration of NO_3^- in the aqueous phase, the extraction performance was almost no change which meant NO_3^- was independent with the extraction process. However, with increasing the concentration of $(C_6mim)^+$ in aqueous phase, the extractability was suppressed at some extent. Therefore, extraction mechanism could be tentatively summarized as the change of cationic constituent of ionic liquid with Eu^{3+}. Furthermore, from the result of slope analysis, it could be confirmed that the formation of a 1:3 complex between Eu^{3+} and $(IL\text{-}TPTNA)^+NTf_2^-$ in this ionic liquid system. In addition, $(IL\text{-}TPTNA)^+NTf_2^-$ showed better preference to heavier lanthanides, and the maximum $SF_{Lu/La}$= 33, which encourages the utilization of $(IL\text{-}TPTNA)^+NTf_2^-$ as an promising ligand in the separation of heavier lanthanides in nitric acid solution.

2. Based on the results from ^1H NMR and FT-IR spectra, it was found that after coordination

with Ln^{3+}, both hard O donor and soft N donor of $(IL\text{-}TPTNA)^{+}NTf_2^{-}$ were involved in the complexation process. UV-vis titration spectra revealed that $(IL\text{-}TPTNA)^{+}NTf_2^{-}$ showed better preference towards Lu^{3+}(heavier lanthanides) than La^{3+}(lighter lanthanides) (log β: $Lu^{3+}>La^{3+}$), which was consistent with the results of mutual separation experiments and ^{1}H NMR titration. By fitting UV-vis titration results with Benesi−Hildebrand equation, 1:1 complex between $(IL\text{-}TPTNA)^{+}NTf_2^{-}$ and Ln^{3+} was supposed to be formed in MeOH solution. As $(IL\text{-}TPTNA)^{+}NTf_2^{-}$ has four pyridine groups which was sensitive to acid. From the curve of pH titration, it was found that all the protonation happened when pH= 2. Therefore, $(IL\text{-}TPTNA)^{+}NTf_2^{-}$ was expected to be used in the pH range till 2. The dependence of the concentration of metal ions EXAFS titration results showed that in the case of Eu^{3+}, hard O donor was dominant, while in the case of Cu^{2+}, soft N donor played a more important role in the complexation process which was in a good agreement with *HSAB* theory. The dependence of pH EXAFS titration results revealed that after complexation with metal ions, the resistance towards acid became stronger. After complexation with Eu^{3+}, even in pH= 2, Eu^{3+} was till combined with $(IL\text{-}TPTNA)^{+}NTf_2^{-}$. However, in the case of only free $(IL\text{-}TPTNA)^{+}NTf_2^{-}$ existed, when pH= 2, all the pyridine groups should be protonated. In the case of Cu^{2+}, even pH= 0.5, Cu^{2+} was still strongly coordinated with $(IL\text{-}TPTNA)^{+}NTf_2^{-}$. On the other hand, without ionic liquid part, TPTNA showed similar EXAFS titration curve with $(IL\text{-}TPTNA)^{+}NTf_2^{-}$, which meant they had similar coordination environment which was consistent with previous studies, and also supported us a way to do theoretical EXAFS fitting.

3. Single crystal of TPTNA with Ln^{3+} was prepared in MeOH solution by using ether as a diffusion anti-solvent. After measurement by using X-ray crystallography method and the later refinement of data, fine structure of single crystal was obtained. It was found that 1:1 complex between TPTNA with Eu^{3+} was formed, seven O donors and three N donors, in total 10 donors, surrounding with one Eu^{3+}. For instance, one amide unit and two pyridine groups participated in the complexation process. Furthermore, theoretical Gaussian calculation was done by using DFT method. The HOMO and LUMO results revealed that pyridine groups in the same side were more active which was in a good agreement with the single crystal structure. Because in the single crystal structure, two pyridine groups from the same side coordinated with Eu^{3+} which can also prove the correction of DFT calculation. In order to have a better understanding of the coordination environment, theoretical fitting was conducted. After simplification of the obtained single crystal structure, making input FEFF file, running FEFF, and fitting, the results showed a similar curve between experimental data and theoretical one. Therefore, based on the difference in bond distances, the coordination environment can be divided into O, N, and C three shells, respectively.

In conclusion, this doctoral thesis systemically introduced a new synthetic procedure to synthesize a novel hydrophobic hard O and soft N donor combined ionic liquid ($(IL\text{-}TPTNA)^{+}NTf_2^{-}$). $(IL\text{-}TPTNA)^{+}NTf_2^{-}$ had a TPEN analogue structure, it showed a good extraction performances of trivalent lanthanides in nitric acid solution. Then, various spectra studies revealed its stability constants and existence conditions in either aqueous or organic phase. Next, X-ray crystallography, DFT calculation, and EXAFS fittings further clarified its coordination environment and extraction mechanism. Soft N and hard O donor combined method as a new kind of strategy has been widely studied in the group separation of MAs and Lns or even in the mutual separation of trivalent lanthanides. But there is still many unknow area should be further clarified to make it as a systematic theory. Therefore, $(IL\text{-}TPTNA)^{+}NTf_2^{-}$ as a new trial by combining ionic liquid with O, N donor also gave an implication for the design of some new kinds of mixed donor ligands. We highly hope $(IL\text{-}TPTNA)^{+}NTf_2^{-}$ one day can play its own role in the practical utilization in the separation of trivalent lanthanides or even in the separation of MAs and Lns.