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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

Doctoral Dissertation

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Chapter 1: General Introduction

"General Introduction" will describe current status of nuclear energy worldwide and in Japan, reprocessing of spent nuclear fuel, as well as the generation and behaviors of minor actinides (MAs) and lanthanides (Lns) in high level liquid waste (HLLW), and also the commonly used methods for their separation. On the other hand, lanthanide (Ln) elements play an important role in the field of advance materials, such as batteries, catalytic converters, permanent magnets etc. trivalent Ln^{3+} ions are dominant species in solution and the solid state in most systems. Owing to the similar ionic radii and coordination numbers, the separation of trivalent Ln^{3+} ions from aqueous phase has been identified as one of the biggest technology challenges. From previous studies, ligands with soft N-donor have been directly used for the extraction of lanthanides in nitric acid solution though solubility and protonation have been frustrating. However, hard O-donor such as amide oxygen donor can provide stronger metal ion binding and lower the basicity of the N-heterocycle, allowing application at a wider pH range. Recently, ligands combining both soft N-donor and hard O-donor have been under intense study concerning extraction and group separation of actinides and lanthanides in the field of nuclear fuel reprocessing process, and also offer considerable potential as extractants for separation of lanthanide elements. A soft N-donor and hard O-donor merged TPEN analogue structure pluses hydrophobic ionic liquid unit will be adopted as the strategy in this doctoral research and then try to evaluate the extraction performances of trivalent Ln^{3+} from the aqueous phase.

Chapter 2: Design, synthesis, and characterization of main ligands

"Design, synthesis, and characterization of main ligands" will introduce that a novel ionic liquid with *N,N,N',N'*-tetrakis(2-pyridylmethyl)-1,3-propanediamine-2-amide structure ((IL-TPTNA)$^{+}$NTf$_2^{-}$) which includes one amide (O-hard donor) and four pyridine (N-soft donor) groups will be synthesized. The synthesis procedures of (IL-TPTNA)$^{+}$NTf$_2^{-}$ will be designed, and optimized carefully. The properties and molecular structures of all the intermediate and final target compounds are also characterized and described in details.

Chapter 3: Extraction performances of (IL-TPTNA)$^{+}$NTf$_2^{-}$ in nitric acid solution

In this chapter, the extraction performances of trivalent lanthanides by (IL-TPTNA)$^{+}$NTf$_2^{-}$ will be investigated in nitric acid solution as an effect of extraction time, pH value, back extraction, slope analysis, concentration of NO_3^{-}, etc. Possible extraction mechanism in this ionic liquid system could be tentatively summarized as the exchange of cationic constituent of ionic liquid with Eu^{3+}. In addition, (IL-TPTNA)$^{+}$NTf$_2^{-}$ showed better preference to heavier lanthanides than lighter ones.

Chapter 4: Preliminary elucidation of complexation environment by different spectroscopy methods

In this chapter, as the synthesized (IL-TPTNA)$^{+}$NTf$_2^{-}$ has two kinds of donors, in

order to make clear whether both of these two kinds of donors are involved in the complexation process or not, FT-IR and ^{1}H NMR experiments of Eu/(IL-TPTNA)$^+$NTf$_2^-$ in the ration of 1:1 will be firstly carried out. By comparing the spectra before and after complexation, it was found that some peak-shifts deriving from NHCO and pyridine groups meant that both amide (hard O-donor) and pyridine groups (soft N-donor) involved in the formation of metal complex. Then the ^{1}H NMR titration experiments of La^{3+} and Lu^{3+} were conducted. The spectra showed similar shift with ^{1}H NMR spectrum from Eu^{3+}. Next, UV-vis titration experiments of La^{3+}, Eu^{3+}, Dy^{3+}, and Lu^{3+} were done and stability constants log β value were calculated from the titration curves. log β of Lu^{3+} was a little bit higher than log β of La^{3+} which can also support the results we obtained above. Based on the titration experiments, Benesi−Hildebrand equation was introduced to theoretically fit the results. And it was found 1:1 complex between (IL-TPTNA)$^+$NTf$_2^-$ and Ln^{3+} was formed in the MeOH solution for all the cases. Then, a hydrophilic (IL-TPTNA)$^+$Br$^-$ was synthesized to conduct pH titration experiments. Its results elucidated that all the pyridines in (IL-TPTNA)$^+$ will be protonated in the highly acidic condition for instance, when pH_{eq} around 2, which is in a good agreement with the results of pH dependence extraction experiment. In order to have a better understanding the properties of the formed complex in MeOH solution, EXAFS titration of (IL-TPTNA)$^+$NTf$_2^-$ with Eu^{3+} and Cu^{2+} were conducted by varying the concentration of (IL-TPTNA)$^+$NTf$_2^-$ or by varying the pH value in MeOH. The results told us in the case of Eu^{3+}, O (H_2O, NO_3^-, amide unit) was the dominant donor (no new peak formed). In the case of Cu^{2+}, N (pyridine group) played an important role in the complexation process (a new peak formed), and these results were in consistent with *HSAB* theory. And after forming complex, Cu/(IL-TPTNA)$^+$NTf$_2^-$ showed better resistance towards acid, from the spectra of pH dependence, even the pH value decreased to 0.5, the spectra still showed no change which can be explained as pyridine groups preferred to priority tightly wrap around Cu^{2+}. However, in the case of Eu^{3+}, when the pH_{eq}= 2, almost all the Eu^{3+} were released. On the other hand, EXAFS titration between (IL-TPTNA)$^+$NTf$_2^-$ and TPTNA were also conducted. By comparing the obtained results, it showed some similarities, for example no second new peak formed. It also showed some differences, in the case of TPTNA, the first peak was shifted a little too higher bond distance area which can be explained the role of pyridine group in TPTNA was more important than in (IL-TPTNA)$^+$NTf$_2^-$. Because the shift of this peak was derived from the interaction between N donor with metal ions from previously published papers. In conclusion, in this chapter, we made clear that both O and N donor were participated in the complexation process.

Chapter 5: Structural elucidation of complexation environment by X-ray crystallography, DFT and EXAFS fitting

In this chapter, we will mainly focus on the elucidation of 3D complexation environment. As (IL-TPTNA)$^+$NTf$_2^-$ was ionic liquid, till now, the reports about the structure of metal single crystal by using ionic liquid were few, especially task specific ionic liquid which was similar with our case. Therefore, in this chapter we only

considered non-ionic liquid part, for instance, TPTNA. Firstly, single crystal of Eu^{3+}/TPTNA was prepared in MeOH solution by using ether as anti-solvent. From the results of X-ray crystallography, it was found that one amide unit, three nitrate and two pyridine groups surrounded one Eu^{3+} and formed a 1:1 complex. As we predicted before, both hard O donors and soft N donors were involved in the complexation process. However, the bond distance between O with Eu^{3+} was shorter than N with Eu^{3+} which meant hard O donor was preferred by Eu^{3+}. Furthermore, theoretical calculation by using DFT method for TPTNA was conducted. By analyzing the calculation results of HOMO and LUMO, it was found that only two pyridines located in the same sides were active. And this result can clearly explain why only two pyridines in the same side grasped with Eu^{3+}. It was consistent with the single crystal structure. On the other hand, in order to have a deep understanding of the coordination environment, theoretical EXAFS fitting was also carried out by simplification of the single crystal structure, making input file, running FEFF and fitting. The experimental results were in good agreement with theoretical fitting and the coordination environment can be divided into three shells, for instance O, N, and C, respectively.

Chapter 6: Conclusions

In this chapter, we will summarize the major results and findings in this doctoral research and we will also give recommendations and hints for further work or implementation of this research.