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Insight of coordination and extraction of yttrium (III) with a new phenoxyacetic acid ionic liquid extractant

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Keywords: Rare earth; Ionic liquid; Extraction; Saponification; Coordination chemistry information

Phenoxyacetic acid type extractants such as sec-octyl phenoxyacetic acid (CA-12), sec-nonyl phenoxyacetic acid (CA-100) and resulting bifunctional ionic liquid extractants, were developed to separate Y from heavy rare earth elements (REEs). With the aim of getting the coordination chemistry information concerning this type of bifunctional ionic liquid extractants involved in rare earth extraction, a CA12 analogue n-octyl phenoxyacetic acid (HOCTPOA) was synthesized and its structure was first characterized by single crystal X-ray diffraction analysis. Then a bifunctional ionic liquid extractant based on HOCTPOA, namely, [N_{1888}][OCTPOA] (where N_{1888} is methyltrioctyl ammonium) was synthesized. The study on extraction behavior of yttrium using [N_{1888}][OCTPOA] from chloride media was conducted through IR, log *D* versus log *C* slope analysis, ESI-MS, EXAFS and DFT studies. X-ray absorption spectroscopy demonstrates that the Y(III) extraction complex with phenoxyacetic acid was formed. Three possible Y(III) coordination cation species were calculated through DFT method and the obtained Y-O bond distances were comparable to the results from EXAFS fitting. A possible structure for the overall extracted complex was proposed, which contributes to getting a better understanding for the extraction with phenoxyacetate type bifunctional ionic liquid.

Introduction

In the periodic table, rare earth elements (REEs) represent a group of 15 lanthanides, scandium and yttrium, which are critical to high-tech industries and clean technologies.[1-6] More and more efforts have been devoted to REEs separation due to increasing global demand for REEs.[7, 8] As one of the most common heavy rare earth elements (HREEs), yttrium is widely used in laser crystal, ceramics, rare earth alloy, and other functional materials.[9-10] As is known to all, it is difficult to separate Y(III) from heavy REEs due to their similar ionic radius (Y^{3+}: 0.88 Å, Ho: 0.89 Å, Er: 0.88 Å, Tm: 0.87 Å, Yb: 0.86 Å, Lu: 0.85 Å).[11]

Phenoxyacetic acid type extractants such as sec-octylphenoxyacetic acid (CA-12) and sec-nonylphenoxyacetic acid (CA-100) developed by Shanghai Institute of Organic Chemistry are a class of organic ligands which have been found to be the most promising for the selective extraction of Y from heavy REEs in recent years. The extraction behavior, kinetics and possible mechanism of this kind of phenoxyacetic acid type extractants with rare earth ions were studied by Li *et al* and coworkers.[12-15] In order to improve the extraction efficiencies between Y and other rare earth ions, double solvent extraction system, namely, one extractant is CA12 and the other extractant is organophosphorus extractants such as C301 and C272 was investigated and applied to the separation process.[16-19]

Solvent extraction based on organic phosphonic acid or carboxylic acid extractants is the widely used and well-established method to separate REEs.[20, 21] However, the acidic extractants are readily to form hydrogen bonded dimers, and needed to be saponified by acid-base neutralization reactions to increase their extractabilities and selectivities by breaking the dimers and eliminating protons.[22] In REEs separation industry, there are several problems of common saponification and extraction processes such as large acid, base consumptions and millions of tons of waste water produced annually.[23] Therefore there is a necessity to develop new methods that selectively extract REEs in a more economical and environmental friendly way. Research reveals that ionic liquid (IL) type saponification is an interesting alternative strategy to overcome the challenges mentioned above.

IL-based extraction is a novel form of solvent extraction that applies ILs instead of VOCs as diluents and/or extractants. ILs are salts, generally in a liquid form below 100 °C. The sustainable properties of ILs make them particularly suitable for solvent extraction.[24-26] Acid-base coupling bifunctional ionic liquids (ABC-BILs), prepared from functional cations and anions were applied to the separations of REEs, offering a promising route to reduce saponification wastewater, increase extractabilities and selectivities.[27] To date, several bifunctional ILs have been synthesized and used in metal extractions, for example, Guo *et al*. synthesized IL extractant for the highly selective extraction and separation of rare earths.[28] Shi *et al.* prepared two ILs and evaluated their extraction efficiencies for the liquid-liquid extraction of lithium ions from aqueous solution.[29] Rout *et al.* synthesized two ILs for liquid-liquid extraction of Nd(III) from nitric acid medium and pointed out the possibility to tune the extractability of metal ions and the selectivity by a proper choice of the ionic liquid cation.[30-31]

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Although several studies about bifunctional ILs in metal ions extraction were reported, further research into the coordination chemistry about this kind of extractants behind solvent extraction was rarely conducted. On the other hand, some phenoxyacetatic acid based bifunctional IL extractants have been synthesized and applied to the rare earth separation. Very recently, the IL type saponification separation processing of [methyltrioctyl ammonium] [sec-octylphenoxy acetate] and [trihexyl(tetradecyl)-phosphonium][sec-octylphenoxy acetate] for yttrium from other heavy REEs has been developed in our laboratory.[32-34] Simplification of reciprocating saponification procedures, avoidance of saponification wastewater and stripping by distilled water are economical and sustainable futures of IL type saponification over common saponification. Also, the IL extractants for synergistic extraction in impregnated resin was studied and revealed higher distribution coefficients and synergistic enhancement coefficients for REEs.[35] Chen *et al.* prepared a novel polymer inclusion membrane composed of bifunctional IL and investigated the preconcentration and separation of heavy rare earth element (HREE) Lutetium (Lu) from dilute solution.[36] The regeneration of the IL after metal extraction was investigated, which implies that bifunctional IL extractants may be applied in a future continuous and sustainable process for metal extraction.[37]

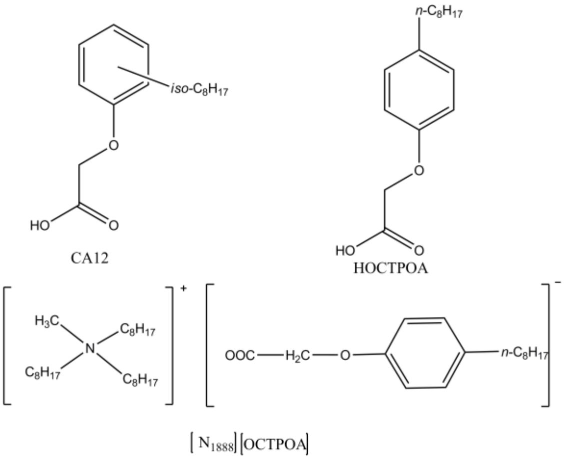

Figure 1. The structures of CA-12, HOCTPOA and [N$_{1888}$][OCTPOA].

Study on coordination chemistry is important to metal ions extraction, as it can provide an explanation for the strengths and selectivities shown by the extractants.[38-41] Peter A. Tasker pointed out that the extraction of metal ions can be achieved through inner-sphere, outer-sphere interactions between extractants and metal species.[42] To our knowledge, the coordination behavior between Y and phenoxyacetic acid extractant together with resulting ABC-BIL was not studied to date. In this paper, the metal extraction for the rare earth ion Y(III) by a bifunctional IL methyltrioctyl ammonium n-octyl phenoxyacetic acid ([N$_{1888}$][OCTPOA]) from chloride media was discussed. This allows a better understanding of the mechanism for the extraction of metal ions from the aqueous with this type of ILs. Structures of CA12, HOCTPOA and [N$_{1888}$][OCTPOA] are shown in Figure 1.

Results and Discussion

2.1. Structure Description for HOCTPOA

The crystal structure for HOCTPOA has been determined by single crystal X-ray diffraction analysis, and revealed that the compound crystallizes in the spacegroup *P-1*. As shown in Figure 2, the C-O bond lengths of the carboxylate groups are 1.2154 and 1.3299 Å, respectively. It is known that organic carboxylic acids readily form dimers through hydrogen bonds, two equivalent HOCTPOA molecules form acid dimer through hydrogen bond with the O$\cdots$O distance of 2.7250 Å.

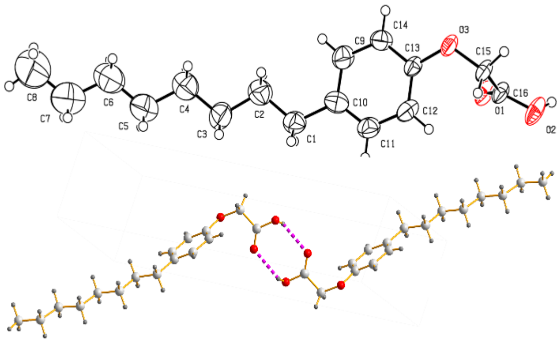

Figure 2. Crystal structure for HOCTPOA and hydrogen-bonded dimer fromed by two equivalent molecules.

IR analysis

As shown in Figure 3, IR spectrum analysis was performed to compare HOCTPOA, [N$_{1888}$][OCTPOA] and [N$_{1888}$][OCTPOA] loaded with Y^{3+}. The disappearance of stretching vibration for C=O group observed at ca. 1717 cm^{-1} indicated the deprotonation of the carboxylate group. The changes of COO$^-$ from 1607 cm^{-1} before extraction to 1610 cm^{-1} after extraction reveals the interactions between the carboxylate group and Y^{3+} ions.[33]

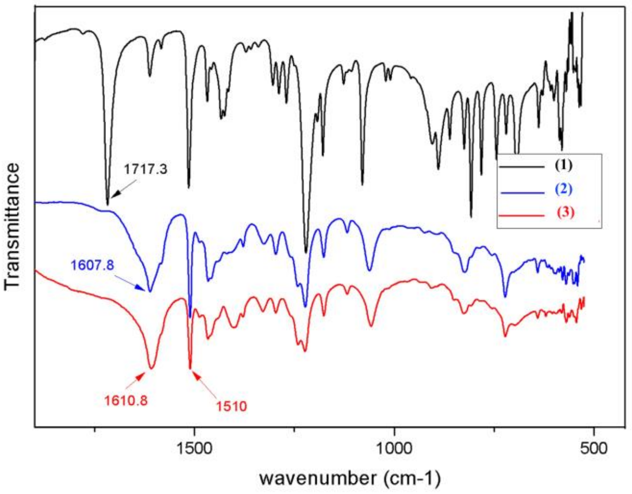

Figure 3. IR spectra of (1) HOCTPOA; (2) [N$_{1888}$][OCTPOA]; (3) 0.4 mol/L [N$_{1888}$][OCTPOA] loaded with YCl$_3$.

Effect of aqueous pH on Y(III) extraction

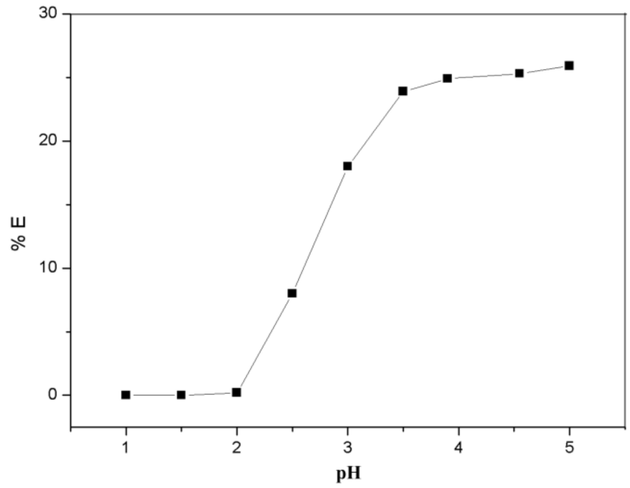

Figure 4. Effect of aqueous phase acidity on the extraction efficiency of Y(III). [Y(III)] = 0.0093 mol/L, $[N_{1888}][OCTPOA]$ = 0.015 mol/L.

As shown in Figure 4, the effect of aqueous pH on the extraction behavior was investigated and the extraction efficiencies of Y(III) were measured at different pH values. The extraction efficiencies of Y(III) increase as the aqueous pH values increase, when the pH values are between 3.5 and 5.0, there are relative higher and stable efficiencies for Y(III) ions.

Effect of Extractant Concentration

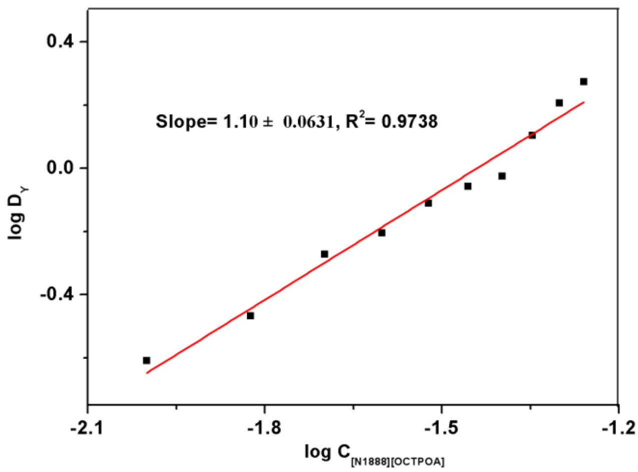

Figure 5. Effect of $[N_{1888}][OCTPOA]$ concentration on the extraction of Y(III). Organic phase: 0.01-0.055 mol/L $[N_{1888}][OCTPOA]$ in heptane. Aqueous phase: 0.0093 mol/L YCl_3; pH = 3.83. O/A = 1:1.

As the IL extractants are diluted in organic solutions and the interactions are relatively weak electrostatic or hydrogen bond actions, which is weaker than coordination action of phenoxyacetic acid between Y(III) ions, so the IL extractants in molecular diluents can be treated as free extractants concerning this extraction system.

The effect of extractant concentration on Y(III) extraction was also investigated, and the result is shown in Figure 5. It showed that the extraction efficiency for Y(III) increased with the increasing of the extractants concentration in $[N_{1888}][OCTPOA]$ extraction systems. The log D against log $C_{[N1888][OCTPOA]}$ showed linear slopes close to 1, which indicates that the stoichiometry of $[N_{1888}][OCTPOA]$ to Y(III) in the organic phase is about 1.

ESI-MS studies

Electrospray ionization (ESI) is a very promising tool for the analysis of IL, metal organic complexes that allows the sample molecules to be transferred directly from the solution to the gas phase by generating charged ions without disrupting metal-ligand bonds.[43]

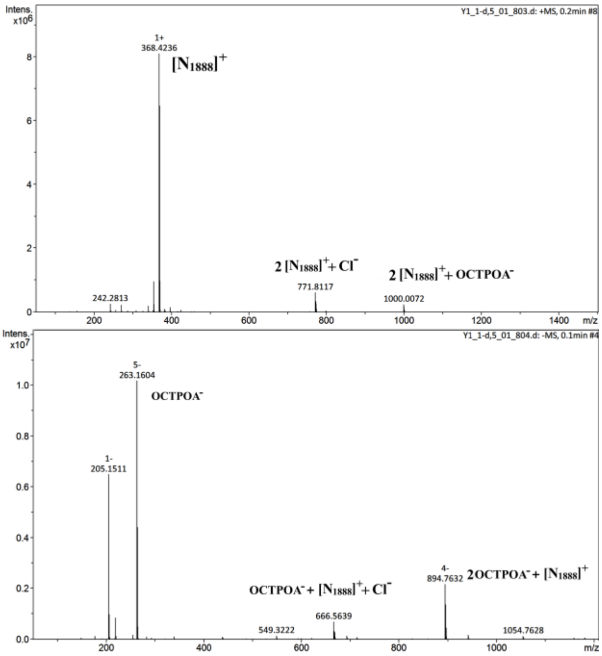

Figure 6. ESI positive and negative ion mass spectrum of the organic phase after extraction equilibrium.

As ESI-MS was effectively used for the analysis of the extraction complex in the solvent extraction, here we tried to use this method to analyze the formed complex between the rare earth Y^{3+} ions and IL extractants $[N_{1888}][OCTPOA]$. However, it is difficult to identify the extraction complex despite trying our best, which may be due to the fact that the relatively low percent $[N_{1888}][OCTPOA]$ IL extractants participation in forming extraction complexes compared to phosphorus extractants with rare earth ions and large quantities of molecular aggregate of IL. How to separate the extraction complexes from ILs may be a possible way to identify the complex with further research. Studies revealed that ILs tend to form molecular aggregates under the vacuum condition in the mass spectrometer, the major *m/z* peaks were molecular aggregates of anions and cations from the ESI-MS analysis. As shown in Figure 6, in the positive mode, the *m/z* peak at 368.4 correspond to the single cation $[N_{1888}]^+$, while the *m/z* peaks at 771.8 and 1000.0 to the aggregates of two $[N_{1888}]^+$ cations, with one Cl^- and one $[OCTPOA]^-$, respectively.

The observed *m/z* peak at 263.1 was the anion of n-octyl phenoxyacetic acid, and the peak found at 666.5 was the aggregate of one $[OCTPOA]^-$, one $[N_{1888}]^+$ and one Cl^-. The major *m/z* peak at 894.7 correspond to the aggregation in the form of two $[OCTPOA]^-$ and one $[N_{1888}]^+$ cation. In previous studies, extraction of the metal cation via a negative complex (e.g., $ZnCl_4{}^{2-}$, $PdCl_4{}^{2-}$) always proceeds via the cation of the IL by the uptake of a negatively charged metal complexes.[44] However this usually occurs at high acid conditions (low pH) and high chloride concentrations. Negative metal complex such as YCl_4^- was not found after an inspection on the negative mode of ESI-MS spectrum as in dilute chloride solutions.

EXAFS Analysis and DFT Calculation of Y(III) Species

In order to obtain the coordination chemistry information involved in solvent extraction such as coordinating atoms, the bond distances between metal ions and neighboring coordination atoms, EXAFS analysis on the organic phase after extraction was conducted. The Fourier transformed $k^2\chi(k)$ EXAFS data and its fitting curves are shown as the solid and dashed line in Figure 7.

Table 1 Fitting Results Deduced from Y K-edge EXAFS Spectra from the organic phase

Shell	CN	R(Å)	σ^2*10^3(Å^2)	ΔE_0(eV)	R factor
Y-O$_1$	2.0±0.2	2.26±0.04	3.0±0.3	-1.8±0.8	
Y-O$_2$	6.0±0.7	2.38±0.04	4.2±0.4	-1.8±0.8	0.010

* CN = Coordination number, R = Bond length, σ^2 = Debye-Waller factor, $\Delta E_0 = E_0$ shift.

As shown in Table 1, EXAFS analysis reveals that there are two kinds of inner sphere coordination oxygen atoms with Y^{3+} ions, one is with relatively shorter Y-O average distance 2.26 Å, which can be ascribed to the oxygen atoms form the phenoxyacetic acid with Y^{3+} ions. The other with relatively longer average bond distance 2.38 Å is from the coordination oxygen atoms of water molecules with Y^{3+} ions, which is consistent with former studies.[45]

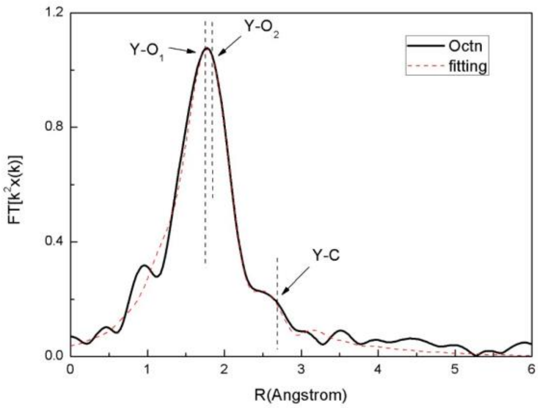

Figure 7. Fourier transform EXAFS spectra of Y-OCTPOA complex octn. k^2: Δk = 3.0 – 11.0Å^{-1}, Δr=1.1 – 3.0 Å, from fitting Y-O nearest neighbors in Y_2O_3 values obtained for $S_o{}^2$ were 0.81.

As the EXAFS technique can give precise mean metal-oxygen bond distances, but not very accurate coordination numbers, we tried to optimize the several possible coordination species. The most stable species of rare earth ions including lanthanide and yttrium cations in solution are found typically in the trivalent oxidation state that allow their diversified coordination number with 7-9 most common in solutions.[46] Therefore, to investigate the possible species, three different Y(III) complexes with coordinated water molecules 5-7, i.e., $[Y(OCTPOA)(H_2O)_5]^{2+}$, $[Y(OCTPOA)(H_2O)_6]^{2+}$ and $[Y(OCTPOA)(H_2O)_7]^{2+}$ were taken into account and optimized at the B3LYP/6-31G(d,p)/RECP level of theory. The optimized structures of Y(III) species and structural parameters such as Y-O bond distances are shown in Figure 8 and Table 1. The Y-O$_c$ average bond lengths in these species are 2.28, 2.30 and 2.34 Å, while the obtained Y-O$_w$ average distances are 2.38, 2.42 and 2.47 Å, respectively. We can see that the results from DFT calculations are comparable to the data from the fitting of EXAFS analysis.

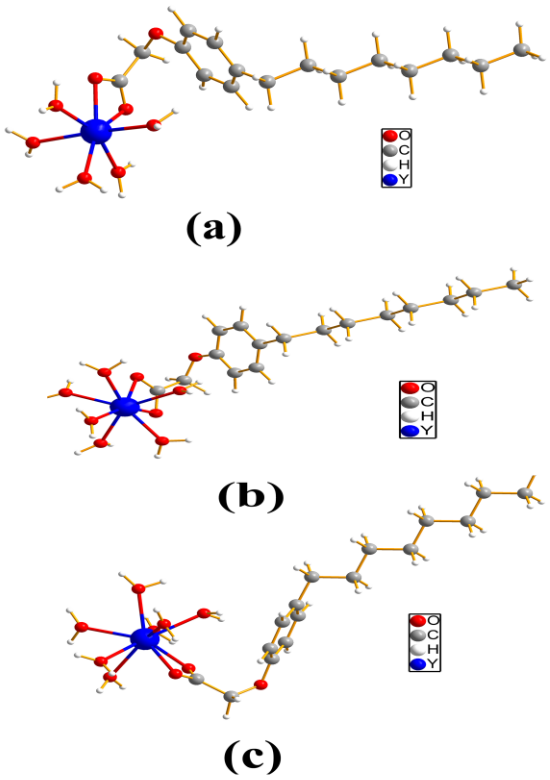

Figure 8. Optimum structures of Y(III) species (a) $[Y(OCTPOA)(H_2O)_5]^{2+}$, (b) $[Y(OCTPOA)(H_2O)_6]^{2+}$ and (c) $[Y(OCTPOA)(H_2O)_7]^{2+}$.

The ion association mechanism of phenoxyacetic acid type IL extractants for REEs(III) extraction in chloride media medium has been pointed out when the $[N_{1888}][CA\text{-}100]$, $[N_{1888}][CA\text{-}12]$ and $[P_{6,6,6,14}][CA12]$ were used as extractants in organic diluents. The final extraction equations (1), (2) and (3) with ionic extractants were written as follows:[32-34]

$$Ln^{3+} + 4[N_{1888}][CA100] + 3Cl^- = LnCl_3 \cdot 4[N_{1888}][CA100] \qquad (1)$$

$$REECl_2^+ + Cl^- + [N_{1888}][CA12] = [N_{1888}]Cl{\cdot}REE[CA12]Cl_2 \qquad (2)$$

$$Y^{3+} + 2.5[P_{6,6,6,14}][CA12] + 3Cl^- = [P_{6,6,6,14}]_{2.5}\,Y[CA12]_{2.5}Cl_3 \qquad (3)$$

In this article, our effort was made to provide insights into the extraction complex structure related to the phenoxyacetic acid bifunctional IL extractants. Based on the former studies, the combination of IR analysis, log *D* versus log *C* slope and EXAFS analysis, we can conclude that each Y^{3+} ion is coordinated by about one $OCTPOA^-$ to form complex cation with charge balanced Cl^- anions. As water is a particularly strong ligand and large hydration energy of REE ions, the Y^{3+} ion is more readily to be coordinated by oxygen atoms from water molecules rather than Cl^- anions in conventional molecular solvents.[47,48] Thus the Cl^- anion, which is co-extracted into the organic phase with IL in the form of molecular aggregates such as $Cl^-\ldots[N_{1888}]^+\ldots[OCTPOA]^-$ and so on, interacts with coordination cation through outer sphere actions.

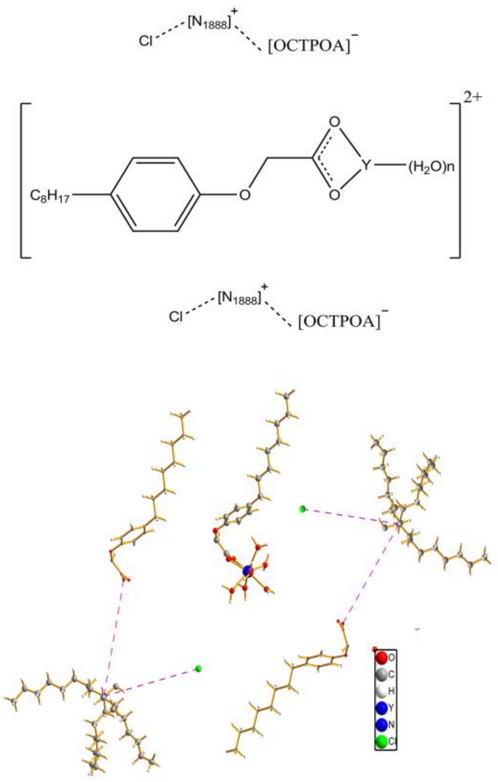

Figure 9. Proposed structure of extraction complex between $[N_{1888}][OCTPOA]$ and Y^{3+} ions.

As shown in Figure 9, the possible extraction complex structure in solution was proposed, the water molecules might be to fulfill the more coordination number of Y^{3+} ions. The whole extraction complex may be a large coordination ion complex. The coordination main part *i.e.*, the inner coordination sphere of Y^{3+} ion was fulfilled by two oxygen atoms from the carboxylic acid and other oxygen atoms from coordinated water molecules, while the Cl^- ions lie in the outer sphere as charge balance ions. As the ESI-MS analysis revealed, the Cl^- might exist in the form of the molecular aggregate such as one $[N_{1888}]^+$, one $OCTPOA^-$ and one Cl^- ion and also on. It is a fact that bifunctional IL extractants can have different extraction behavior compared to conventional organic compounds, both cations and anions have distinct influence on the extraction properties of IL extractants. Studies in our case revealed that Y(III) ions were extracted into organic phase through the coordination to phenoxyacetate anion, while one role of the amine cation played was dragging the Cl^- to organic phase to maintain charge balance. As coordination chemistry concerning IL extraction with metal ions was also important and less reported in this insight, our research contributes to getting a better understanding on extraction process about this type of IL extractant from a different view.

Conclusions

In conclusion, a new phenoxyacetic acid type bifunctional IL extractant was synthesized and its extraction behaviour with Y^{3+} ions was studied. Based on the information obtained from the IR, ESI-MS, log *D* versus log *C* slope analysis and EXAFS analysis, the whole extraction complex was deduced to be a large coordination ion complex. The structural parameters Y-O bond distances obtained from DFT calculations for three possible Y coordination cation species were comparable to the EXAFS fitting results. The studies tried to provide useful information for an improved understanding of the fundamental aspects of the Y(III) extraction with phenoxyacetic acid type bifunctional ILs extractants, which contributes to developing the sustainable and efficient separation technology based on IL type saponification strategy for REEs.

Experimental Section

Reagents and Instruments: Trioctylmethylammonium bromide ($[N_{1888}]Br$) was purchased from Yixing Kai Lida Chemical Co., Ltd (China). An anion-exchange resin (Dowex Monosphere 550A (OH)) was obtained from the Dow Chemical Company. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra of the octyl phenoxyacetic acid and its ABC-BILs were obtained in $CDCl_3$ with an AV III-500 Bruker spectrometer. The extracting phases were prepared by dissolving the extractants in heptane. The yttrium oxide was purchased from Fujian Changting Golden Dragon Rare-Earth Co., Ltd (China). Stock solutions of YCl_3 were prepared by dissolving yttrium oxide (>99.99%) in concentrated hydrochloric acid and diluted with distilled water. Thermo scientific iCAP 6500 series plasma-atomic emission spectroscopy (ICP-AES) was used to determine the concentrations of REEs of aqueous phase in extraction procedure. IR spectra were measured with a Nicolet iS50 spectrometer, when the IR measurement was conducted, the solution of 0.012 mol/L Y(III) in organic phase was used. Electrospray ionization mass spectrometry (ESI-MS) was performed on a Finnigan LCQ mass spectrometer using CH_3CN as mobile phase.

Synthesis of 4-Octyl Phenoxyacetic Acid (HOCTPOA): A solution of 0.01 mole of the 4-octyl phenol, 0.02 mole of KOH in 30 ml of ethanol was heated to boiling. The appropriate bromocarboxylic acid (2.06 g, 0.01 mole), dissolved in 30 ml of ethanol, was added dropwise, the resulting solution was heated under reflux overnight. The reaction mixture was cooled, acidified with dilute HCl, and concentrated under reduced pressure. The residue was extracted with ether, and after being dried, the ether was removed to give a waxy residue. The product was recrystallized from petroleum ether to afford 0.8 g HOCTPOA as white crystals. (mp 91-92 ºC) ^{1}H NMR δ (500 MHz, $CDCl_3$) 0.88 (t, 3H), 1.25-1.27 (m, 10 H), 1.55-1.57 (m, 2H), 2.55 (t, 2H), 4.65 (s, 2H), 6.85 (d, 2H), 7.11 (d, 2H). ^{13}C NMR (500 MHz, $CDCl_3$): 172.50, 155.33, 136.82, 129.50 (2C), 114.52 (2C), 65.10, 35.05, 31.88, 31.62, 29.47, 29.26 (2C), 22.67, 14.10. Anal. calcd for $C_{16}H_{24}O_3$ (%): C, 72.69; H, 9.15; Found: C, 72.38; H, 9.63.

Synthesis of [N_{1888}][OCTPOA]: A solution of [N_{1888}]OH in 20 ml methanol was prepared from 0.269 g of [N_{1888}]Br (0.6 mmol) using a Dowex Monosphere 550A (OH) anion exchange resin. 0.1586 g of octyl phenoxyacetic acid (0. 6 mmol) was added to the [N_{1888}]OH solution. The mixture was then stirred at room temperature for 6 h until the solution became neutral. The methanol and water were distilled off with a IKA RV10 rotary evaporator, and the product was dried at 70 ºC under vacuum for 12 h to yield [N_{1888}][OCTPOA] as a yellow viscous liquid (0.35 g, yield: 92.3%). ^{1}H NMR δ (400 MHz, $CDCl_3$) 0.85-0.88 (t, 12 H), 1.24-1.29 (m, 40 H), 1.55-1.57 (m, 8H), 2.48 (t, 2H), 3.20 (s, 3H), 3.21-3.25 (m, 6H) 4.40 (s, 2H), 6.83 (d,2H), 7.00 (d, 2H). ^{13}C NMR (500 MHz, $CDCl_3$): 173.38, 157.14, 134.40, 128.91 (2C), 114.58 (2C), 67.92, 61.26 (3C), 48.69, 35.10, 31.9, 31.8, 31.64 (3C), 29.70 (3C), 29.50, 29.37, 29.29, 29.13 (3C), 29.01 (3C), 26.31 (3C), 22.67, 22.57 (3C) 14.09, 14.03 (3C). Anal. calcd for $C_{41}H_{77}NO_3$ (%): C, 77.91; H, 12.28; N: 2.22 Found: C, 77.38; H, 11.96; N, 2.98

Extraction Procedure

Extraction experiments were performed by contacting equal volumes of organic phase with aqueous solution for 30 min in a vibrating mixer at 30 °C. The concentration of the REEs in the aqueous phase was determined using ICP-OES after centrifugation at 2500 rpm for 5 min. All the concentration values of the REEs in extraction procedure were measured in duplicate and the uncertainty was within 5%. The extraction efficiency (E), distribution ratio (D) were defined as follows:

$$E\% = \frac{[M]_t - [M]_a}{[M]_t} \times 100\% \qquad (4)$$

$$D = \frac{[M]_t - [M]_a}{[M]_a} \qquad (5)$$

where $[M]_t$ and $[M]_a$ represent initial and final concentrations of Y(III) in the aqueous phase.

Solution and Sample Preparation for EXAFS, Data Collection and Analysis

The extraction experiments were performed by contacting 5 mL of heptane containing the extractant (0.05 M) with 5 mL of aqueous 0.018 M YCl_3 (pH=3) for 30 min in a vibrating mixer at 30 ºC. The aqueous phase was separated, and concentration of the REE in EXAFS analysis was determined by standard EDTA titration. The organic phase was separated for EXAFS analysis.

X-ray absorption fine structure (XAFS) data at the Y K-edge was collected in fluorescence mode on BL14W at the Shanghai Synchrotron Radiation Facility (SSRF, China). The electron beam energy is 3.5 GeV, and the mean stored current is 200 mA. The source of BL14W is a 38-pole wiggler device with maximum magnetic field of 1.2 T. The station was operated with a Si (111) double crystal monochromator. The extended XAFS (EXAFS) signals were extracted from the absorption raw data by using the IFEFFIT package.[49]

General procedures for X-ray crystallography

Crystals for single-crystal X-ray analysis were obtained for n-octyl phenoxyacetic acid as described in the synthesis procedure. The data was collected using a graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Bruker AXS-KAPPA APEX II diffractometer. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all observed reflections. The structures were solved and refined using direct methods the SHELXTL software package.[50] CCDC 1497757 contains the supplementary crystallographic data for this paper.

DFT Calculation Details

The calculation for structural optimization of proposed Y-complex was carried out with the Gaussian 09 program using Dell PowerEdge T630, 2 CPU Intel E5-2640 V32.6 GHz, 32 GB RAM computational sources.[51] The geometric configuration of Y(III) species was optimized in the gas phase using the B3LYP hybrid exchange-correlation functional, viz., Becke’s three-parameter exchange functional (B) and the Lee-Yang-Parr correlation (LYP) functional, and a 6-31G(d, p) basis set for C, H, O atoms.[52, 53] While the quasi-relativistic effective core potentials (RECPs) of Dolg et al. (ECP28MWB) was used for Y.[54] The optimized geometry was confirmed to be the minimum energy point with no imaginary vibrations by vibrational frequency analysis.

Acknowledgments

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