Extraction of lanthanides from nitric acid solution usingisobutyl-BTP/ionic liquid system Postprint

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Date: 2023-06-18T00:00:00+00:00

Abstract

The extraction behavior of lanthanides (La, Eu, Dy, Lu) from HNO3 solution was investigated using a novel extraction system with a hydrophobic ionic liquid as diluent and isobutyl-BTP as extractant. Compared with the isobutyl-BTP/cyclohexane extraction system, the application of ionic liquid as the extracting phase afforded unprecedented enhancement in the extraction performance of isobutyl-BTP for lanthanides. It was found that the isobutyl-BTP/[Cnmim][NTf2] extraction system is favorable for achieving efficient extraction under low acidity conditions (<0.1 M). Among all the isobutyl-BTP/ [Cnmim][NTf2] (n=2, 6, 8) systems, the isobutyl-BTP/[C2mim][NTf2] extraction system exhibited the best extraction performance and fastest extraction kinetics toward Dy3+, with extraction completing within 5 min. The extraction was spontaneous and endothermic, with temperature being favorable for extraction. The transfer of lanthanides in the isobutyl-BTP/[C2mim][NTf2] extraction system proceeded via a cation exchange mechanism, in contrast to the neutral complex extraction observed in the cyclohexane system.

Full Text

Preamble

Extraction of Lanthanides from Nitric Acid Solution Using Isobutyl-BTP/Ionic Liquid System

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(Received May 20, 2014; accepted in revised form August 9, 2014; published online December 20, 2014)

The extraction behavior of lanthanides (La, Eu, Dy, Lu) from HNO_3 solution was studied using a novel extraction system with hydrophobic ionic liquid as diluent and isobutyl-BTP as extractant. Compared with the isobutyl-BTP/cyclohexane extraction system, application of ionic liquid as the extracting phase provided unprecedented enhancement of the extraction performance of isobutyl-BTP for lanthanides. It was found that the isobutyl-BTP/[C mim][NTf_2] extraction system is favorable for achieving good extraction under low acidity conditions (< 0.1 M). Among all the isobutyl-BTP/[C mim][NTf_2] (n = 2, 6, 8) systems, the isobutyl-BTP/[C_2mim][NTf_2] extraction system provides the best extraction performance and fastest extraction kinetics, reaching equilibrium within 5 min for Dy^{3+}. The extraction is spontaneous and endothermic, and increasing temperature is beneficial for extraction. The transfer of lanthanides in the isobutyl-BTP/[C_2mim][NTf_2] extraction system proceeds via a cation exchange mechanism, in contrast to the extraction of neutral complexes in the cyclohexane system.

Keywords: Lanthanides, Extraction, Ionic liquids, isobutyl-BTP
DOI: 10.13538/j.1001-8042/nst.26.S10305

Ionic liquids have been identified as ideal alternative solvents in liquid-liquid extraction due to their unique properties such as negligible vapor pressure, good thermal and chemical stability, and excellent dissolving ability [?]. It has also been noted that lanthanide cations can be extracted from aqueous phase into the ILs phase through a cation exchange mechanism without adding acids [?]. Dietz et al. [?] reported that 1-amyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imides ([C_5mim][PF_6]) solution containing dicyclohexano-18-crown-6 showed a high distribution coefficient of strontium at low acidity as the cation exchange between [C_5mim]$^+$ and Sr^{2+}. Nakashima et al. [?] reported that 1-butyl-3-methyl-imidazolium hexafluorophosphate [C_4mim][PF_6] solution containing 3 mM octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide could extract 90% of Ce^{3+} from deionized water, since the [PF_6]$^-$ anion plays a key role in the electrical neutralization of the $Ln^{3+} \cdot 3$CMPO complex. Therefore, the application of ILs can construct a low acidity extraction system to enhance the stability of the extraction system.

[Figure 1: see original paper] Chemical structures of isobutyl-BTP and [C mim][NTf_2].

∗ Supported by the National Natural Science Foundation of China (Nos. 91126006 and 11475112), the Ph.D. Programs Foundation of Ministry of Education of China (No. 20130073120051), and the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning

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In the present study, an extraction system consisting of 2,6-bis(5,6-dihexyl-1,2,4-triazin-3-yl)pyridine (isobutyl-BTP) as extractant (Fig. 1(a)) and 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C mim][NTf_2]) as diluents (Fig. 1(b)) was designed. The extraction behavior of several lanthanide ions (La, Eu, Dy, Lu) from low acidity HNO_3 solution was studied. The isobutyl-BTP/cyclohexane system was investigated for comparison purposes.

II. EXPERIMENTAL

A. Materials

The isobutyl-BTP (> 95%) was synthesized according to Ref. [**?**]. [C mim][NTf_2] (purity > 99%) was purchased from Lanzhou Greenchem ILs, LICP, CAS, China (Lanzhou, China). No impurities were detected using ^{1}H NMR spectrometry. The other organic and inorganic compounds were commercial products of reagent grade and used without further purification. Stock solutions of La^{3+}, Eu^{3+}, Dy^{3+} and Lu^{3+} were prepared by dissolving their nitrate salts in HNO_3 solution.

B. Method

1. Solvent extraction The extraction phase (2.0 mL) containing 25 mM isobutyl-BTP was prepared by dissolving isobutyl-BTP in [C mim][NTf_2], and the aqueous solution (2.0 mL) containing La^{3+}, Eu^{3+}, Dy^{3+} and Lu^{3+} (2 mM for each species) was prepared in HNO_3 medium at concentrations of 0.01, 0.1, 0.5, 1, 2 and 3 M. The extraction experiments were conducted by contacting the extraction phase with aqueous solution for designated time in a constant temperature incubator shaker which maintained a thermostated water bath at 25 °C with a rotating speed of 120 rpm, followed by centrifuging for 3 min to ensure complete phase separation.

After phase separation, the aqueous solution was diluted with deionized water, and the lanthanide concentration in the diluted aqueous solution was measured by Prodigy high dispersion inductively coupled plasma atomic emission spectrometer (ICPS-7510, SHIMADZU, JPN). The extraction experiments for lanthanides using the isobutyl-BTP/cyclohexane extraction system were carried out under the same conditions.

The distribution ratios (D) and extraction efficiencies (E) were calculated using Eqs. (1) and (2), respectively, where M represents the cation species in aqueous phase, the subscript org/aq denotes organic phase/aqueous phase, while the subscript "i/f" designates the initial/final concentration of metal ions in the diluted solution.

$$D = \frac{[M]_{org}}{[M]_{aq}}$$

$$E = \frac{[M]_{aq,i} - [M]_{aq,f}}{[M]_{aq,i}} \times 100$$

2. UV-visible analysis of cation in the IL The content of $[C_2mim]^+$ in aqueous phase after extraction was quantified using UV-Visible spectrophotometry (SHIMADZU UV-3600 PC spectrophotometer). Calibrations were performed using standards with a series of initial concentrations of $[C_2mim]Cl$ dissolved in water. The characteristic band was selected at 210 nm due to its relatively high signal intensity.

3. Back extraction experiment of isobutyl-BTP/$[C_2mim][NTf_2]$ against Dy^{3+} Extraction experiments were conducted as described above. After extraction of Dy^{3+} at 0.01 M HNO_3, the mixture was centrifuged to separate the aqueous phase and IL phase, and then the IL phase (1 mL) was contacted with back extraction agent (1 mL) of H_2O, 1 M HNO_3, 3 M HNO_3, 0.01 M DTPA (Diethylene triamine pentaacetate acid) and 0.5 M thiourea under the same conditions for 48 h. The concentration of Dy^{3+} was analyzed by ICPS-7510 (SHIMADZU, Japan).

III. RESULTS AND DISCUSSION

Firstly, we investigated the extraction of lanthanides using ILs alone in the absence of isobutyl-BTP and found that the ILs alone can hardly extract lanthanides. This is similar to the work reported by Shimojo et al. [**?**]. However, in a solubility experiment, we found that [C mim]$[NTf_2]$ (n = 2, 6, 8) exhibited excellent solubility for isobutyl-BTP.

A. Extraction of Dy^{3+} in different extraction systems

The distribution ratio of Dy^{3+} ion (D_{Dy}) as a function of HNO_3 concentration for the isobutyl-BTP/[C mim]$[NTf_2]$ systems and the isobutyl-BTP/cyclohexane system is shown in Fig. 2 [Figure 2: see original paper].

In the cyclohexane system, D_{Dy} increased with HNO_3 concentration, indicating that the ${NO_3}^-$ anion enhances extractability due to neutral complex formation. The extraction mechanism can be expressed as Eq. (3) [**?**]:

$$M^{3+}_{(aq)} + 3NO^-_{3(aq)} + 3BTP_{(org)} \rightleftharpoons M(BTP)_3(NO_3)_{3(org)}$$

In the isobutyl-BTP/[C mim]$[NTf_2]$ systems, D_{Dy} decreased rapidly with increasing HNO_3 concentration from 0.01 M to 1 M, where it began to increase slightly. The curves differ from each other because of the mechanism transition depending on acidity variation. H^+ is a competitive species in cation exchange, hence higher D_{Dy} is observed with lower H^+ concentration; but when the H^+ concentration is great enough to restrain the cation exchange, neutral extraction becomes the dominant mechanism. Consequently, D_{Dy} increases slightly with acidity, just as in the cyclohexane system.

Based on the above discussion, the HNO_3 concentration of 0.01 M was used in the following experiments using the isobutyl-BTP/[C mim][NTf_2] system.

B. Extraction kinetics of isobutyl-BTP/[C mim][NTf_2] extraction system

Extraction kinetics reflect basic properties of the extraction system, so isobutyl-BTP/[C mim][NTf_2] extraction experiments with different contact times were carried out. In the isobutyl-BTP/[C_2mim][NTf_2] system, a significant advantage in extraction kinetics was observed (Fig. 3 [Figure 3: see original paper]). Its extraction kinetics for Dy^{3+} reached equilibrium in 5 min, about 1000 times faster than that in the isobutyl-BTP/[C mim][NTf_2] (n = 6, 8) systems, which required dozens of hours to reach equilibrium. This indicates that both hydrophobicity and viscosity of imidazolium are impeditive to cation exchange [**?**]. Longer alkyl chain of IL would improve the hydrophobicity and viscosity. Therefore, [C_2mim][NTf_2] was chosen as the diluent for the following lanthanide extraction.

C. Determination of thermodynamic parameters

The temperature effect on the extraction of Dy from 0.01 M HNO_3 using 20 mM isobutyl-BTP/[C_2mim][NTf_2] system was studied. As shown in Fig. 4 [Figure 4: see original paper], D_{Dy} increased with temperature, indicating an endothermic extraction process.

The change in enthalpy (ΔH) during extraction can be calculated by the Van't Hoff equation:

$$\Delta H = -2.303R\frac{\Delta \lg D}{\Delta(1/T)}$$

A plot of log D vs. 1/T gives a straight line with a slope of -ΔH/2.303R, while the change in Gibbs free energy (ΔG) can be calculated by:

$$\Delta G = -2.303RT\lg K$$

The change in entropy (ΔS) at a particular temperature can be calculated by:

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

From Eqs. (4), (5) and (6), the values of ΔH, ΔG and ΔS are 28.91, 19.86 and 30.37 kJ/mol, respectively. Therefore, the extraction is spontaneous and endothermic, and increasing temperature is beneficial for extraction.

D. Extraction mechanism of Ln using isobutyl-BTP/[C_2mim][NTf_2] system

In order to verify the proposed cation exchange mechanism, we carried out extraction experiments in deionized water by mixing aqueous solutions of $EuCl_3$ with [C_2mim][NTf_2]. Since $DyCl_3$ has poor water solubility, and ultraviolet absorption of $NO_3{}^-$ has strong interference on [C_2mim]$^+$ cation, we chose $EuCl_3$ for this investigation. As shown in Fig. 5 [Figure 5: see original paper], calibration curves of [C_2mim]$^+$ were used to measure the concentration of [C_2mim]$^+$ in the aqueous phase transferred from [C_2mim][NTf_2]. We measured the Eu^{3+} concentration in [C_2mim][NTf_2] transferred from the aqueous phase and [C_2mim]$^+$ in the aqueous phase transferred from [C_2mim][NTf_2]. The results were plotted against each other in Fig. 6 [Figure 6: see original paper], showing a linear relationship with a slope of 2.84. Due to experimental error, we considered the slope to be 3. This indicates that a cation exchange mechanism is occurring with three cations from the IL involved. Therefore, the extraction equilibrium equation at low HNO_3 concentration can be suggested as:

$$[Ln]^{3+}_{(a)} + 3BTP_{(o)} + 3[C_{2mim}]^+ \rightleftharpoons [Ln(BTP)_3]^{3+}_{(o)} + 3[C_{2mim}]^+$$

In the equation, the stoichiometric ratio of Dy^{3+} to BTP is based on previous investigation [**?**].

E. Extraction of Ln in isobutyl-BTP/[C_2mim][NTf_2] system

To assess the extraction performance of the isobutyl-BTP/[C_2mim][NTf_2] extraction system for lanthanides, ion species of La^{3+}, Eu^{3+}, Dy^{3+} and Lu^{3+} were employed as light, middle, middle, and heavy lanthanides, respectively. As shown in Table 1 , the order of extraction efficiency for lanthanides was $Eu^{3+} > Dy^{3+} > Lu^{3+} > La^{3+}$, indicating that the isobutyl-BTP/[C_2mim][NTf_2] system is inclined to extract Eu^{3+} and Dy^{3+}. Therefore, we suppose that the ionic sizes of dysprosium and europium are particularly suitable for coordination.

TABLE 1 . Extraction efficiency of several lanthanides using isobutyl-BTP/[C_2mim][NTf_2] system at 0.01 M HNO_3

Ionic radius (Å)	Extraction efficiency (%)
(Table content would appear here)	

F. Back extraction

The stripping of Dy^{3+} from [C_2mim][NTf_2] was carried out to further understand recycling. Several complexing agents were chosen, including 0.01 M DTPA, 0.5 M thiourea and high concentration HNO_3. Pure water was chosen as a comparison. As shown in Table 2 , Dy^{3+} was completely stripped at 3 M HNO_3, while other back extraction agents did not function. Considering the extraction behavior discussed above, we think that the Dy-isobutyl-BTP complexation ($[Dy(BTP)_3]^{3+}$) in the IL phase is unstable at high acidity, hence the stripping of Dy ion at 3 M HNO_3. Perhaps this cannot be called back extraction. Further efforts will be made to find a good back extraction agent for Dy without causing instability of $[Dy(BTP)_3]^{3+}$.

TABLE 2 . Stripping efficiency of Dy^{3+} from isobutyl-BTP/[C$_2$mim][NTf$_2$] system using various stripping solutions

Stripping solution	Stripping efficiency (%)
0.5 M Thiourea	(Data would appear here)

IV. CONCLUSION

A novel extraction system based on isobutyl-BTP/[C mim][NTf$_2$] was developed for lanthanide extraction. The system provided high extraction performance for lanthanides compared with cyclohexane. Among all isobutyl-BTP/[C mim][NTf$_2$] systems (n = 2, 6, 8), the isobutyl-BTP/[C$_2$mim][NTf$_2$] system provides the best extraction performance and the fastest extraction kinetics, reaching equilibrium within 5 min for Dy^{3+}. It was found that the isobutyl-BTP/[C$_2$mim][NTf$_2$] system is inclined to extract at low acidity conditions, and can be stripped at high HNO_3 concentration. The extraction mechanism based on cation exchange was reasonably proposed for the novel extraction system. In addition, Dy^{3+} was found to be favorably extracted in the current isobutyl-BTP/[C$_2$mim][NTf$_2$] extraction system. The extraction is spontaneous and endothermic, and increasing temperature is beneficial for extraction. Therefore, this extraction system is effective for use under low acidity conditions. These unique properties of the IL-based extraction system may help us design new separation processes for hydrometallurgy industry or advanced nuclear fuel cycle applications in the future.

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Note: Figure translations are in progress. See original paper for figures.