S. Afr. J. Chem., 2015, **68**, 69–75,
<http://journals.sabinet.co.za/sajchem/>.

Extraction of Cerium (IV) Using Di–n-butylsulfoxide in Chloroform from Nitric Acid and Determination with Arsenazo (III) as Chromogenic Reagent

Muhammad Haleem Khan*, Khurram Liaqat, Muhammad Hafeez, Srosh Fazil and Muhammad Riaz

[1]*Department of Chemistry, University of Azad Jammu & Kashmir, Muzaffarabad, Pakistan.*

Received 17 October 2014, revised 12 January 2015, accepted 20 January 2015.

ABSTRACT

A new and advantageous extraction procedure was developed for extraction of cerium (IV) from nitric acid with di-*n*-butylsulfoxide (DBSO) in perchloric acid. The extracted Ce (IV) was determined spectrophotometrically using 0.01 % solution of arsenazo-III in 3 M per-chloric acid. Various parameters such as equilibration time, metal ion concentration, effect of temperature and diverse ions on the extraction of the Ce (IV) were established. U (VI), Th (IV) and Pb (II) interfere whereas only phosphate and fluoride suppress the extraction among anions. The stoichiometric composition of the cerium complex with DBSO was determined by slope analysis and found to be 1:4. The process of extraction was found to be exothermic. Deionized water was the most appropriate solvent for back extraction of cerium. This method is easier and more sensitive than many of the reported procedures.

KEYWORDS

Cerium, extraction, DBSO, perchloric acid, arsenazo-II.

1. Introduction

Cerium is the most abundant among rare earth metals and is extracted from monazite, allanite and bastnasite minerals.[1] Very pure cerium is used for the production of nuclear power and as a catalyst in nuclear and automobile industries, as an alloy with chromium; in microwave devices, television sets, lasers besides some important uses in environmental pollution assessment, agronomy and biochemistry. In addition to this, many cerium compounds has been found important for biomedical applications.[2]

Atomic absorption spectroscopy (AAS) and inductively coupled plasma optical emission spectroroscopy (ICP OES) techniques are not promising for direct determination of cerium and a prior separation is required.[3–6] The extraction chemistry of cerium has been studied and different extractants such as lueco xylene cyanol (FF), N-phenylbenzo-18-crown-6-hydroxamic acid, tri-n-butyl phosphate (TBP), resorcinarene-N-fenil-aceto-hydroxamic acid, di-(-2-ethylhexyl) 2-ethylhexyl phosphonate (DEHEHP), cyanex 923, 2-ethylhexyl hydrogen 2-ethylhexyl phosphonate, N,N′-Dimethyl-N,N′-diphenyl-pyridine-2, 6-dicarboxyamide (DMDPhPDA), tridodecylamine (TDA), 1-[thenoyl-(2)]-3-3-3-trifluoroacetone (HTTA), di (2-ethylhexyl) phosphoric acid (HDEHP) and tricaprylmethyl-ammonium chloride (TCMA) have been used.[7–22] In addition to this the extraction chemistry of cerium has also been explored with N-*n*-octylaniline, acetophenone 2,5 dihydroxy, semicarbazone, Variamine blue, 2,4, dihydroxy benzophenoe benzoic hydrazone, 2,6-dibromo-4-chloro carboxyarsenazo, 4-dimethyl amino-azo benzene-arsenic acid, pyrogallol red, dibromo-*p*-methyl chloro sulphanzo, propionil promazine phosphate, N-P-chloro-phenyl-*p*-methoxy hydroxamic acid, tributylphosphine oxide (TBPO), tricaprylmethylammonium chloride, calix [IV] resorcinarene acid derivative [C_4RAHA], butyl phosphate, 3-phenyl-4–benzoyl-5-isoxazolone (HPBI), bifunctional ionic liquids, octacarboxymethyl-C-methylcalix , organophosphorous extractants, malachite green, arsenazo (III).[23–43] However, there are certain limitations associated with extraction of cerium such as interference of different ions, co-extraction, emulsion formation, use of high reagent concentrations less sensitivity and expensive back-stripping reagents.

In this communication, we report the extraction of Ce (IV) with DBSO in nitric acid using arsenazo-III as chromogenic reagent. The proposed method is highly suitable as almost quantitative extraction of cerium is possible. Higher amounts of cerium can be stripped back to deionized water thus the process is economically more favourable.

2. Experimental

2.1. Reagents, Solutions and Apparatus

All chemicals used were of analytical grade. Cerium sulphate stock solution (1000 μg mL^{-1}) was prepared in 2 M sulphuric acid. Solutions of arsenazo-III were prepared by dissolving the measured amount of disodium salt of the compound in $HClO_4$. Salting-out agent solution (0.01 molar) was prepared by adding 3.75 g of $Al(NO)_3.9H_2O$ in deionized water and further dilutions were made to prepare solutions of required concentrations. Potassium phosphate, potassium fluoride, sodium sulphate, sodium cyanide, sodium chloride and sodium thiosulphate solutions were made by adding 100 mg of each salt in deionized water and making up the total volume to 10 mL. Uranyl nitrate, thorium nitrate, zinc chloride, lead nitrate solutions were made by adding 100 mg of respective salt in deionized water and making up the total volume of 10 mL. 7.5 M nitric acid solution was made by taking 425 mL (15.7 M) nitric acid and diluting it to

* To whom correspondence should be addressed: E-mail: mriazm1@yahoo.com

ISSN 0379-4350 Online / ©2015 South African Chemical Institute / http://saci.co.za/journal
DOI: http://dx.doi.org/10.17159 /0379-4350/2015/v68a11

1000 mL with deionized water and further dilutions were made from that. Nitric acid (0.1 M) and ammonium hydroxide (0.1 M) solutions were made by taking 100 mL of each from 1 M respective stock solutions and making up dilution to 1000 mL with deionized water. Di-*n*-butylsufoxide solution (2 M) was prepared by dissolving 32.4 g of it in chloroform and making the total volume 100 mL. Spectral measurements were obtained using digital spectrophotometer (Shimadzu Japan, model-1601) with an automatic recording device.

2.2. General Extraction Procedure

Known amount of the cerium sulphate solution was taken in a 100 mL glass beaker and was heated (to near dryness) on an electric hot plate. On cooling, 3.0 mL of the 3.0 M HNO_3 was added to it; 2.0 mL of this solution was pipetted out in a screw-capped (18 × 125 mm) culture tube and the remaining 1.0 mL in the 50.0 mL beaker was treated as reference. The aqueous phase was equilibrated with an equal volume of 1.0 M DBSO in chloroform for 5 min and phase separation was achieved with centrifugation. One mL of aqueous solution was pipetted out in another beaker and was heated to near dryness. 3.0 mL of the arsenazo-III (0.01 %) in 3.0 M $HClO_4$ was added on cooling and was mixed thoroughly for colour development. The reagent blank was prepared under identical conditions but without metal ions. The absorbance measurement was made at 658 nm against the reagent blank (Fig. 1). The peak 1 shows the complex. (All presented data are an average of triplicate measurements.)

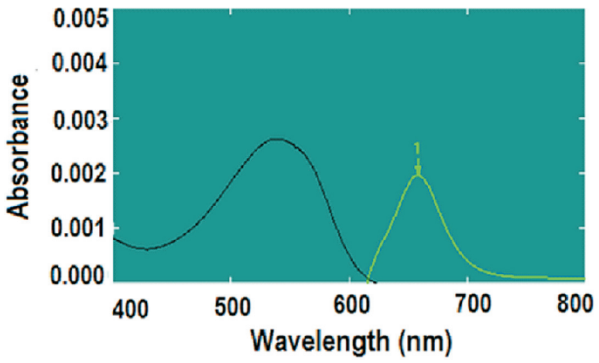

Figure 1 Absorption spectra of Ce complex.

The distribution ratio (kd) was calculated with the following equation:

$$Kd = (Ct - Cex)/Cex \quad (4.1)$$

In this equation, Ct and Cex indicate the total concentration of the cerium in aqueous phase before and after extraction, respectively.

$$\% \text{ extraction} = Kd \times 100 / (Kd + 1)$$

Accuracy of the extraction method under study has been explored by extracting cerium contents (1000–5000 μg mL^{-1}) from Ce (IV) standard solution (Table 1). A significant decrease in percentage deviation was observed while increasing cerium concentration. It was noted that loading capacity of DBSO for cerium is quite high to extract the metal ions present in the concentration range studied but decrease in percentage deviation of cerium at its high concentration was probably due to fluctuations caused by the dilution at spectrophotometric step. Another possible reason for the decreasing percentage deviation might be the higher metal ion concentration as nitric acid competition for extractant decreases and maximum extraction of cerium occurs which resulted an increase in the expected error. Therefore, we noted that in this extraction procedure, lower concentration of metal ions gives better results.

Table 1 Accuracy of the developed procedure.*

Ce added/μg mL^{-1}	Ce found/μg mL^{-1}	± Deviation/percentage
100	65	–35
1000	960	–4.0
2000	1978	–1.1
3000	2988	– 0.4
5000	4990	– 0.2

* Data the average of three measurements.

3. Results and Discussion

3.1. Effect of Nitric Acid Concentration

Dependency of percentage extraction of cerium with different concentrations of nitric acid (using 1.0 M DBSO in chloroform) was studied (5 min shaking time). Equal volume (2.0 mL of each) of organic and aqueous phases was equilibrated. An abrupt increase in the percentage extraction of cerium with increasing concentration of nitric acid reaching a maximum value (76 % for 3.0 M HNO_3) was observed (Fig. 2). Further increase of the nitric acid concentration caused a decrease in the percentage extraction of cerium in the range of 0.5 to 7.5 M. At lower acid strength, percentage extraction was higher due to mild competition between cerium and acid for complexation with DBSO. This might be due to the fact that increasing acid concentration decreases free DBSO concentration thus leading to a stronger competition between metal (cerium) and acid (HNO_3) for complexation with the extractant. Coordination of DBSO with HNO_3 results into (nDBSO.mHNO_3) adduct. Thus after reaching a maximum (with 3 M nitric acid), percentage extraction decreases with increasing acid concentration.

3.2. Effect of Equilibration Period

The shaking time duration affects the extraction of cerium (IV) using 1.0 M DBSO and has been studied while keeping all the parameters constant under previously optimized experimental conditions (Fig. 3). The results are indicative of a sharp enhancement in percentage extraction by increasing shaking period (for 5 min) and then a decrease with increasing shaking time. This can be explained on the basis of the fact that equilibration between cerium and DBSO in this system reaches equilibrium saturation with a high rate constant that no further increase in extraction was observed (after 5 min shaking time). Therefore, it appears that equilibrium for $Ce(NO_3)_4$.nDBSO is faster than that of $Ce(NO_3)_4$.nDBSO.mHNO_3. After 5 min more of the latter forms, resulting in less efficient extraction of the metal. In conclusion, disparity of shaking time indicated that a single extraction with DBSO (1.0 M) in chloroform for a maximum of 5 minfrom HNO_3 (3.0 M) solution is appropriate for cerium extraction (up to 75 %). The concentration range of Ce was 10.77×10^{-3} to 3.56×10^{-3} mol dm^{-3}.

3.3. Effect of Extractant Concentration

The impact of extractant concentration was explored by changing the concentration from 0.3 to 2.0 M DBSO using chloroform as diluent. All other parameters were kept constant under previously optimized experimental conditions. A curve was constructed between different molarities of DBSO solution versus extraction of cerium (Fig. 4). Maximum percentage extraction was with 1.0 M DBSO and then a decrease was noted. Two factors are potentially responsible for the decrease in the

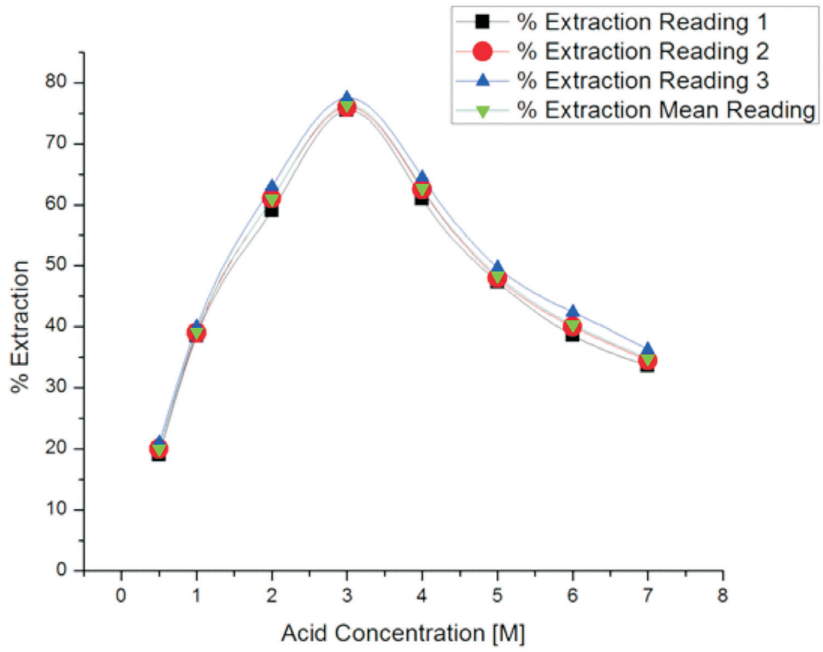

Figure 2 Effect of nitric acid (3.0 M) concentration on the extraction of Ce in the presence of DBSO (1.0 M), (n = 3).

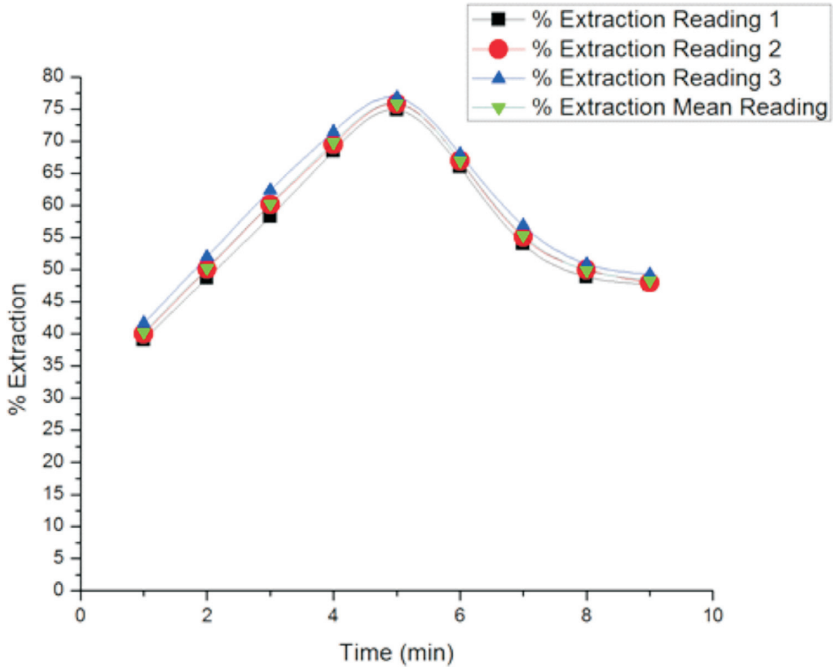

Figure 3 Effect of shaking time on the extraction of Ce (0. 1 M DBSO in chloroform and 3.0 M HNO_3), (n = 3).

percentage extraction of cerium (with increased concentration of extractant). Firstly, due to extraction of more nitric acid by higher concentration of DBSO solution, aqueous acid concentration decreases resulting into a lower K_d value of cerium. Secondly, the volume of the organic phase increases due to more extraction of acid by higher DBSO concentration thus decreasing cerium concentration in the organic phase. Therefore, 1.0 M DBSO (solution in chloroform) was selected as maximum concentration of the extractant for quantitative cerium (IV) extraction. The concentration range of Ce was 10.77×10^{-3} to 3.56×10^{-3} mol dm^{-3}.

3.4. Effect of Metal Ion Concentration

The extraction potential of DBSO (0.2 to 2 M solution in chloroform) from 3.0 M HNO_3 solution for varying concentration of cerium (3.56×10^{-3}–10.77×10^{-3} mole dm^{-3}) was studied keeping other parameters constant (Table 2). These results indicate a quantitative extraction of cerium (IV) for concentration range studied. Percentage extraction increases with increasing DBSO concentration thus indicating the high loading capacity, which is very encouraging for the proposed extraction method.

Since DBSO makes coordinate covalent bonds with $Ce(NO_3)_4$, it is therefore to vary the concentration to fully understand its role in the extraction process.

3.5. Effect of a Salting-out Agent

Varying concentrations of aluminum nitrate $Al(NO_3)_3.9H_2O$ were used during extraction of cerium keeping other parameters constant (Table 3). On adding nitrate (from aluminum nitrate), the extraction efficiency was increased probably due to partici-

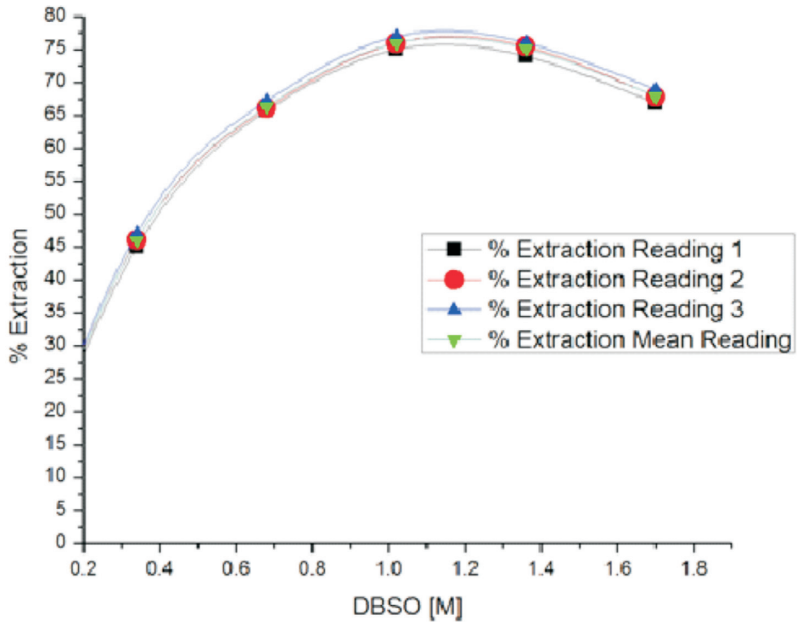

Figure 4 Effect of DBSO (in chloroform) and 3.0 M HNO_3 concentration on extraction of Ce, (n = 3).

Table 2 Effect on of concentration on Ce extraction (1 M DBSO in chloroform and 3 M nitric acid), (n = 3).

[Ce]/mol dm^{-3}	DBSO/mol d^{-3}	Extraction/percentage
3.56×10^{-3}	0.1	55.0
4.28×10^{-3}	0.2	61.5
4.99×10^{-3}	0.3	66.0
5.70×10^{-3}	0.4	71.8
6.42×10^{-3}	0.6	75.0
7.13×10^{-3}	0.8	75.8
7.85×10^{-3}	1.0	77.2
8.56×10^{-3}	1.0	78.9
9.27×10^{-3}	1.1	77.0
9.99×10^{-3}	1.1	76.5
10.77×10^{-3}	1.2	75.4

* Data the average of three measurements.

pation in the metal solvation process. However, with low acid concentration, the nitrates increase extraction by common ion and salting-out effects.

3.6. Effect of Anions

The effect of various anions such as PO_4^{-3}, F^-, SO_4^{-2}, CN^-, Cl^- and $S_2O_3^{-2}$ on the extraction of cerium was studied by mixing the sodium or potassium salts (Table 4). Anions such as PO_4^{-3} and F^- have reduced the percentage extraction while sulphate, cyanide, chloride and thiosulphate have comparatively less effect. The serious interference of PO_4^{-3} and F^- was due to complex formation with Ce in aqueous solution. The formation constants of these ions with cerium are higher than with nitrate. These ions act as masking agent for cerium extraction. Therefore, interfering anions must be separated from the aqueous phase prior to extraction.

Table 3 Salting-out agent effect on Ce extraction (1 M DBSO, 3 M nitric acid, 10.77×10^{-3} to 3.56×10^{-3} mol dm^{-3} cerium).

Salting-out agent/mg 3 mL^{-1}	Extraction/%
Nil	75.0
50	75.1
70	75.3
100	75.9
150	76.4
200	77.4
250	77.4

* Data the average of three measurements.

Table 4 Anions effect on Ce extraction (1M DBSO, 3 M nitric acid, 10.77×10^{-3} to 3.56×0^{-3} mol dm^{-3} cerium).

Anions added/10 mg mL^{-1}	Extraction/%	± Deviation (from normal value)
Nil	75.0	Nil
Phosphate	25.5	–66.0
Fluoride	32.4	–56.8
Sulphate	68.5	–8.70
Cyanide	71.2	–5.10
Chloride	72.1	–3.30
Thiosulphate	73.3	–2.30

*Data the average of three measurements.

3.7. Effect of Cations

The effect of various cations such as uranium, thorium, zinc, lead, aluminum, and sodium on the extraction of cerium was studied (Table 5). The data indicated that lead, thorium and

Table 5 Various cations effect on Ce extraction (1 M DBSO, 3 M nitric acid, 10.77×10^{-3} to 3.56×10^{-3} mol dm^{-3} cerium).

Cations added/10 mg mL^{-1}	Extraction/%	Deviation (from normal value)
Nil	75.0	Nil
U(IV)	65.0	–13
Th(IV)	67.0	–11
Zn(II)	74.0	–1
Pb(II)	71.0	–5
Al(III)	76.0	+ 1
Na(I)	73.9	–1.5

* Data the average of three measurements.

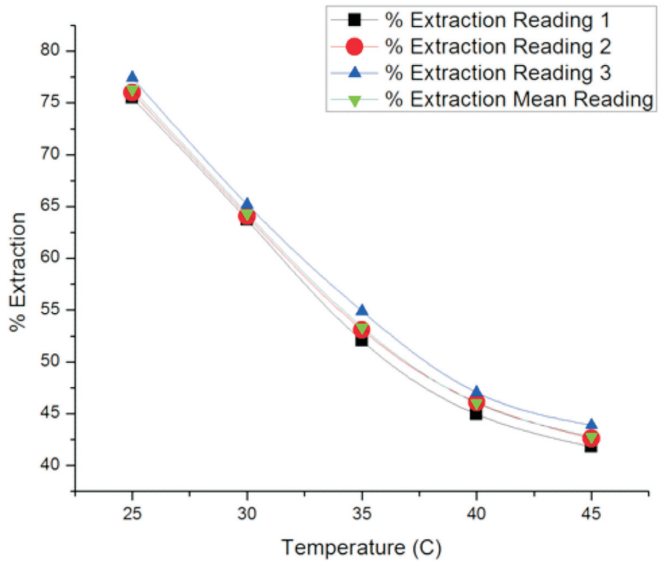

Figure 5 Effect of temperature on the extraction of Ce (1M DBSO, 3 M nitric acid, 10.77×10^{-3} to 3.56×10^{-3} mol dm^{-3} cerium).

uranium have reduced the normal percentage extraction of cerium while cations such as zinc and sodium have comparatively less effect. An increase in percentage extraction of cerium was noted for Al (III).

3.8. Effect of Temperature

The temperature effect (25 to 50 °C) on the extraction process was explored. The percentage extraction of Ce (IV) has an inverse relation with increasing temperature. Thus, an increase in temperature does not favour the extraction of cerium because of competition by the other extractable species (Fig. 5). Hence, a lower temperature is favourable for Ce (IV) extraction process used herein.

3.9. Stoichiometric Composition of the Extracted Complex

Stoichiometric composition of the cerium DBSO complex was investigated using a slope analysis method (using 3.0 M HNO_3 as aqueous phase). Different concentrations of DBSO solution (in chloroform) were used (Figs 6, 7). The following theoretical equation was used to establish the extraction mechanism.

$$Ce^{4+} + 4NO_3^{2-} + nDBSO \leftrightarrow Ce(NO_3)_4 \cdot nDBSO$$

$$K_{eq} = \frac{Ce(NO_3)_4 \cdot nDBSO]_{org}}{[Ce^{4+}]^2_{aq}\,[NO_3^-]^4_{aq}\,[DBSO]^n_{org}}$$

As:

$$K_d = \frac{Ce(NO_3)_4 \cdot nDBSO]_{org}}{[Ce^{4+}]^2}$$

where n is the number of DBSO molecules.

$$K_{eq} = \frac{K_d}{[NO_3^-]^4_{aq}\,[DBSO]^n_{org}}$$

By taking log on both sides of equation:

$$\log K_{eq} = \log K_d - \log[NO_3^-]^4_{aq} - \log[DBSO]^n_{org}$$

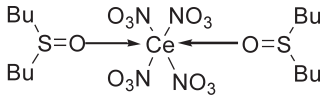

Figure 6 Proposed structure of Ce (IV) complex.

By rearranging

$$\log K_d = \log K_{eq} + 4\log[NO_3^-] + n\log[DBSO]$$

$$\log K_{eq} + 4\log[NO_3^-] = \text{constant} = K]$$

$$\log K_d = K + n\log DBSO \qquad 5.1$$

Equation 5.1 represents a straight line equation giving the slope equal to *n* and the intercept equal to logKeq + 4 $\log(NO_3)^-$. By using the equation (1), a log–log plot of the distribution ratio *versus* DBSO concentration at constant concentrations of metal ion and nitric acid and is shown in Fig. 7. Slope (2) suggested that two molecules of DBSO are attached with $Ce(NO_3)_4.2DBSO$.

Cerium preferably coordinates with coordination number 6 or 8 but higher coordination numbers are also possible.[44] If it is assumed that nitrate ions in this complex are linked to cerium in a mono-dentate mode, then presence of four mono-dentate nitrate groups and the additional two mono-dentate sulfoxide molecules with cerium in the resulting complex give a coordination number of 6.

3.10. Stripping of Extracted Cerium

Aqueous solutions of nitric acid (0.1 M), ammonium hydroxide (0.1 M) and deionized water were used for cerium stripping from the organic phase (DBSO in chloroform, and ammonium hydroxide solution (0.1 M) was found to be the most effective (Table 6). Recovery of cerium with water and 0.1 M HNO_3 was found to be 89 % and 75 %, respectively. Deionized water was finally chosen as stripping agent based upon the economic consideration and extraction effectivity of cerium from organic phase.

Table 6 Stripping of extracted cerium with different stripants (1M DBSO, 3 M nitric acid, 10.77×10^{-3} to 3.56×10^{-3} mol dm^{-3} cerium).

	1st Stage/%	2nd Stage/%	3rd Stage/%	Total recovery/%
0.1 M NH_4OH	71	15	3.5	89.5
Deionized Water	68	17	4.0	89.0
0.1 M HNO_3	54	20	1.0	75.0

*Data the average of three measurements.

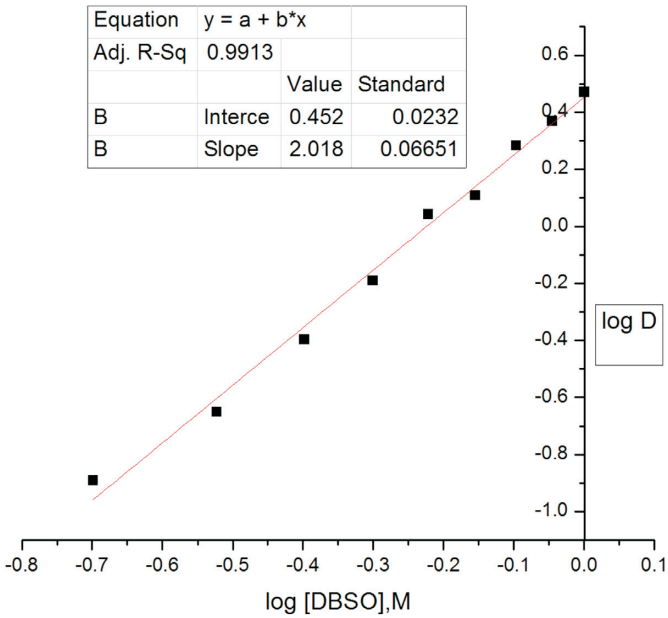

Figure 7 Stoichiometric composition of extracted complex (black square represents the relationship between log[DBSO],M and logD while red line represents trend line).

Table 7 Recycling of the extracting agent (1 M DBSO, 3 M nitric acid, 10.77×10^{-3} to 3.56×10^{-3} mol dm^{-3} cerium).

No. of cycles	Percentage extraction
1	75.0
2	74.6
3	74.2
4	73.0

* Data the average of four measurements.

3.11. Recycling of the Extracting Agent

The recycling ability of DBSO (in chloroform) for the extraction of cerium was studied and the process was repeated four times and results are shown in Table 7. Extracting potential of the organic solvent has been checked out and found to be the same after back extraction without any deterioration.

4. Conclusion

This method for the cerium extraction is significantly simple, sensitive, selective and reproducible for rapid determination of cerium (IV). Almost quantitative extraction of cerium (IV) from 3.0 M nitric acid solution could be achieved with 1.0 M DBSO solution in chloroform. Higher amount of cerium (89 %) can be stripped back into the deionized water.

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