LIQUID – LIQUID EXTRACTION OF CERIUM(IV) FROM SALICYLATE MEDIA USING N-N-OCTYLANILINE IN XYLENE AS AN EXTRACTANT

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ABSTRACT

Extraction behaviour of Ce(IV) from salicylate medium has been studied with the using N-n-octylaniline in xylene as an extractant. Cerium(IV) was completely recovered from the organic phase using 2.0 M hydrochloric acid and determined spectrophotometrically as complex with Arsenazo III. The influence of equilibrium pH, extractant concentration, stripping agents, equilibration time, nature of diluents, and diverse ions on the extraction of Ce(IV) was investigated. The stoichiometry of the extracted species was determined on the basis of slope analysis. The separation of Ce(IV) was carried out from some associated metals like U(VI), Th(IV), La(III), Y(III), Zr(IV), Nb(V), Gd(III) and Nd(III). The method presented is simple, reproducible, rapid and has been successfully applied for the determination of Ce(IV) in synthetic mixture, semiconductor films and monazite sand.

Keywords: Solvent extraction, Ce(IV), N-n-octylaniline, sodium salicylate

INTRODUCTION

Among rare earths, cerium is the most widely distributed element averaging 22 ppm in the earth's crust [1]. Compounds of cerium are used in various fields such as magnetic, catalysts, polishing powder, and ceramic technology. Solvent extraction is reported to be one of the most effective technique to extract cerium(IV) [2]. The main source of cerium are the minerals like monazite (Ce, La, Th, Nd, Y) PO₄ and bastnasite (Ce, La, Y) CO₃F in which cerium coexists with other rare earth (RE) elements.

A number of extractants such as di-(2-ethylhexyl)2-ethylhexylphosphonate (DEHEHP) [2-4], cyanex 923 [5-8], lueco xylene cyanol FF [9], 2-ethylhexyl hydrogen 2-ethylhexyl phosphonate (KSM-17) [10], N, N'-Dimethyl-N,N'-diphenylpyridine-2, 6-dicarboxamide (DMDPhPDA) [11], N-phenylbenzo-18-crown-6- hydroxamic acid [12], 1-octyl-3-methylimidazolium hexafluorophosphate [13], high molecular weight carboxylic acids [14], N-phenyl-1-(1,2-methanofullerene C₆₀) 61-formohydroxamic acid [15], tri-n-butyl phosphate (TBP) [16], tridodecylamine (TDA), 1-[thenoyl-(2)]-3-3-trifluoroacetone (HTTA), di (2-ethylhexyl) phosphoric acid (HDEHP) and tricaprylmethylammonium chloride (TCMA) [17], calyx [4] resorcinarene-N-fenil-acetohydroxamic acid [18], have been used for the extraction and separation of Ce(IV). However, these methods have limitations such as interference of different ions, emulsion formation, co-extraction, and use of high reagent concentrations.

In the present study the extraction of Ce(IV) was carried out from weak organic acid media, sodium salicylate, instead of mineral acids such as HCl, H₂SO₄, HNO₃ and HClO₄. The advantage of organic acid over mineral acid is the facility to control the concentration of complexing ligand, the ease of adjustment of pH due to wide difference in pH at which various metals form anionic complexes with high stability. The method also becomes environmental friendly. N-n-octylaniline, a secondary amine has been explored as an extractant for Ce(IV) in salicylate media. N-n-octylaniline has its potential advantages with respect to low cost, completely miscible with diluents, low aqueous solubility and high purity.

The present work deals with a study of the extraction of cerium(IV) and its separation from some commonly associated metal ions, such as U(VI), Th(IV), Nb(V), Zr(IV), Y(III), Nd(III), La(III), and Gd(III) from salicylate media with N-n-octylaniline. The developed method was applied for the recovery of cerium(IV) from synthetic mixtures, semiconducting film and monazite sand.

EXPERIMENTAL

Apparatus

An Elico digital spectrophotometer model SL -171 with 1cm quartz cells was used for absorbance measurements. pH measurements were carried out using an Elico digital pH meter model LI-120

Reagents

Standard Cerium(IV) solution

The stock solution of Ce(IV) was prepared by dissolving 4.257 g of Cerium ammonium sulphate in one liter water containing 2 mL of concentrated sulphuric acid. The solution was standardized titrimetrically [19]. The working solution was prepared by appropriate dilution of the stock solution with distilled water.

Arsenazo III

Arsenazo III (S.D.Fine Chemicals) was prepared as a 0.05% aqueous solution for the spectrophotometric determination of Ce(IV).

N-n-octylaniline

The extractant N-n-octylaniline was prepared by the method of Gardland et al [20] and its solutions were prepared in xylene.

All other chemicals used in this work were of AR grade. Double distilled water was used throughout the procedure.

General extraction and determination procedure for Cerium(IV)

An aliquot of 50 µg Ce(IV) solution was mixed with a sufficient quantity of sodium salicylate (0.200 g) to make its concentration 0.05 M in a total volume of 25 mL of the solution. The pH of the aqueous solution was adjusted to 8.5 with dilute hydrochloric acid and sodium hydroxide solution. The solution was then transferred to a 125 mL separating funnel and shaken with 10 mL of 0.3 M N-n-octylaniline in xylene for 5 min. After separating the two phases, the aqueous phase was discarded and the organic phase was stripped with three 10 mL portions of 2 M hydrochloric acid solution. The stripped aqueous phase was equilibrated with 5 mL of xylene to remove the traces of dissolved amine and evaporated to moist dryness. The slightly acidic solution was transferred to a 25 mL volumetric flask followed by 2 mL of acetate buffer solution (pH 2.6) and 2 mL of 0.05 % Arsenazo III, diluted to the mark and Ce(IV) was determined spectrophotometrically [21] with Arsenazo III at 660 nm against the reagent blank in the reference cell. The amount of Ce(IV) in the solution was calculated from the calibration curve.

RESULTS AND DISCUSSION

Effect of pH

The effect of pH on the extraction of Ce(IV) with 0.13 M N-n-octylaniline in xylene was studied. The percentage extraction of Ce(IV) increased with the increase in pH of the aqueous phase up to pH 9.0 and after that decreased. This shows that the equilibrium in the pH range 8.0-9.0 is favourable for the formation of ion-pair complex from sodium salicylate media (Fig. 1). Thus the optimum pH 8.5 was selected for efficient extraction of Ce(IV).

Fig 1. Extraction behaviour of Ce(IV) as a function of pH from 0.05 M sodium salicylate with 0.13 M *N-n*-octylaniline. (Ce(IV) = 50 µg)

Effect of reagent concentration

The concentration of *N-n*-octylaniline in xylene was studied by extracting a fixed amount of Ce(IV) with varying amount of *N-n*-octylaniline at the pH 8.5. It was found that 10 mL solution of 0.13 M *N-n*-octylaniline in xylene was quite needed for the complete extraction of Ce(IV) (Table 1). However lower concentration of *N-n*-octylaniline reduces the percentage extraction while an excess of reagent, there was no adverse effect on extraction.

Table 1. Effect of *N-n*-octylaniline Concentrations on the Extraction of Ce(IV)

<i>N-n</i> -octylaniline, (M)	Percentage extraction, (%E)	Distribution ratio, (D)
0.00	0.00	0.00
0.0022	52.3	4.8
0.0044	66.6	7.7
0.022	75.4	9.3
0.031	78.7	10.2
0.043	80.3	41.3
0.087	94.3	77.0
0.11	100.0	∞
0.13	100.0	∞
0.17	100.0	∞
0.22	100.0	∞
0.30	100.0	∞
0.43	100.0	∞
0.65	100.0	∞

Ce(IV) = 50 µg, pH = 8.5, Aq: Org ratio = 25:10, Sodium salicylate = 0.05 M, Strippant = 2.0 M Hydrochloric acid (3 x 10 mL), Equilibrium time = 5 min.

Effect of weak organic acid concentration

The extraction of Ce(IV) from 0.01 - 0.1 M of various weak organic acids were studied with 0.13 M *N-n*-octylaniline in xylene (Table 2). The extraction of Ce(IV) was found to be quantitative in the range of 0.04 M - 0.07 M sodium salicylate. Hence, further studies were carried out using 0.05 M of sodium salicylate as the aqueous phase. While the extraction of Ce(IV) was found to be incomplete in sodium succinate, sodium malonate and sodium citrate media.

Table 2. Extraction of Ce(IV) as a function of Weak Organic Acid Concentrations.

Acid Concentration, (M)	Sodium salicylate		Sodium succinate		Sodium malonate		Sodium citrate	
	% E	D	% E	D	% E	D	% E	D
0.01	35.6	1.4	39.4	1.6	15.4	0.5	30.5	1.1
0.02	51.3	2.6	53.3	2.9	25.8	0.9	25.4	0.9
0.03	92.5	10.8	69.3	5.6	32.5	1.2	12.1	0.3
0.04	100.0	∞	76.4	8.1	40.0	1.7	5.7	0.2
0.05	100.0	∞	87.9	18.1	50.8	2.6	—	—
0.06	100.0	∞	61.7	4.0	57.4	3.4	—	—
0.07	100.0	∞	58.9	3.6	61.5	4.0	—	—
0.08	78.7	9.2	54.8	3.0	48.1	2.3	—	—
0.09	73.2	6.8	49.0	2.4	45.2	2.1	—	—
0.1	60.1	3.8	40.0	1.7	31.0	1.1	—	—

Ce(IV) = 50 µg, pH = 8.5, Aq: Org ratio = 25:10, *N-n*-octylaniline = 10 mL 0.13 M in xylene, Strippant = 2.0 M Hydrochloric acid (3 x 10 mL), Equilibrium time = 5 min.

Effect of solvents

Extraction with high molecular weight amine extractant depends upon the nature of diluent. In order to study the role of diluents during extraction of Ce(IV), various organic solvents such as xylene, benzene, toluene, methyl *iso*-butyl ketone (MIBK), kerosene, chloroform, 1, 2-dichloroethane, carbon tetrachloride were examined as diluents for *N-n*-octylaniline (Table 3). Quantitative extraction of Ce(IV) was possible using xylene as a adequate solvent for *N-n*-octylaniline. Hence 0.13 M *N-n*-octylaniline in xylene was used in throughout the studies. The non-polar organic solvents with a low dielectric constant had better extractability for Ce(IV). However, no particular reason can be given for the comparatively lower 'D' values for Ce(IV) using kerosene and carbon tetrachloride as an diluents.

Table 3. Effect of Diluents on Extraction of Ce(IV).

Diluent	Dielectric constant, ε	Percentage extraction, (%E)	Distribution ratio, (D)
Benzene	2.28	75.8	7.8
Toluene	2.38	97.7	102.1
Xylene	2.30	100.0	∞
Kerosene	1.80	38.2	1.5
Carbon tetrachloride	2.24	50.5	2.5
Chloroform	4.40	89.9	22.1
Amyl alcohol	13.90	72.0	6.5
1,2-Dichloroethane	10.5	85.1	14.2
MIBK	13.11	79.4	93.7
<i>n</i> -Butanol	17.80	78.3	9.0

Ce(IV) = 50 µg, pH = 8.5, Aq: Org ratio = 25:10, Sodium salicylate = 0.05 M, Strippant = 2.0 M Hydrochloric acid (3 x 10 mL), Equilibrium time = 5 min, *N-n*-octylaniline = 10 mL 0.13 M in xylene.

Nature of extracted species

The stoichiometry of the complex species was determined by using log D-log C plots. A plot of the distribution ratio log D versus the log C of the salicylate concentration at a fixed pH 6.0 and 10.0 and 0.13 M *N-n*-octylaniline concentrations gave a slope of 1.86 and 2.12 respectively (Fig. 2). A graph of log D_[Ce(IV)] versus log C_[N-n-octylaniline] at fixed salicylate concentration and pH 6.0 and 10.0 gave a slope of 1.73 and 1.94 respectively (Fig. 3). This indicates a molar ratio of 1:2 Ce(IV) with respect to salicylate and that of *N-n*-octylaniline is also 1:2. Thus the extracted species was calculated to be an ion association complex with the probable composition 1:2:2 (metal: acid: extractant). The probable mechanism of extracted species as follows,

Fig 2. Log-log plot of $\log D_{[Ce(IV)]}$ against $\log C_{[sodium\ salicylate]}$ at fixed *N-n*-octylaniline concentration (0.13 M).

Fig 3. Log-log plot of $\log D_{[Ce(IV)]}$ against $\log C_{[N-n-octylaniline]}$ at fixed sodium salicylate concentration (0.05 M).

Effect of stripping agent

Stripping is the reverse of the extraction, so it should be promoted by those factors that affect the extraction negatively such as acidic and salt media. Alkalies were unsuccessful because the anion complex adhered in the organic medium under these conditions. The stripping percentage was calculated relative to the initial amount of Ce(IV) in the pregnant organic solution. Mineral acids such as hydrochloric acid, nitric acid, perchloric acid sulphuric acid and acetic acid were used as stripping agents for back extraction of Ce(IV) from the organic phase. The results are summarized in table 4. It was observed that quantitative recovery was achieved with three 10 mL portion of 1.5 to 2.5 M hydrochloric acid as a stripping agent. In practice, three 10 mL portion of 2.0 M hydrochloric acid was found to be suitable stripping agent. In other mineral acids back extraction is not successful because it might be due to no complete dissociation of ion-pair complex.

The stripping of Ce(IV) with mineral acid such as HCl took place accordingly the following equation (4).

Table 4. Effect of Stripping agent on Recovery of Ce(IV)

Molarity, (M)	HCl Recovery, %	HClO ₄ Recovery, %	HNO ₃ Recovery, %	CH ₃ COOH Recovery, %	H ₂ SO ₄ Recovery, %
0.1	78.6	67.4	66.0	67.6	54.4
0.5	80.6	61.8	88.2	80.1	63.8
1.0	96.2	55.0	71.3	80.1	79.1
1.5	100.0	49.4	66.3	69.4	91.7
2.0	100.0	45.0	58.0	67.0	90.0
2.5	100.0	40.6	53.9	66.7	82.1
3.0	84.7	34.4	53.9	64.2	74.7
3.5	78.9	27.4	40.6	63.3	67.7
4.0	66.8	25.3	38.5	59.0	57.7
5.0	62.7	18.5	34.6	54.5	43.3

Strippant Recovery, %

- 1) Water 7.9
- 2) Acetate buffer (pH = 3.42) 89.5 (pH = 5.57) 85.0

Ce(IV) = 50 µg, pH = 8.5, Aq: Org ratio = 25:10, Sodium salicylate = 0.05 M,

Equilibrium time = 5 min, *N-n*-octylaniline = 10 mL 0.13 M in xylene.

Period of equilibration

The extraction of Ce(IV) was examined for various periods of equilibration from 0.16 to 20 min. with *N-n*-octylaniline. Quantitative extraction of Ce(IV) was found within 4 min. There was no adverse effect on the extraction yield up to 20 min. with either of the extractant. Hence 5 min. period for equilibration was recommended in order to ensure the complete extraction of metal ion.

Effect of aqueous to organic volume ratio

The extraction of Ce(IV) was carried out in different aqueous to organic volume ratios in the range 300-10 mL of 0.05 M aqueous sodium salicylate medium with 10 mL 0.13 M *N-n*-octylaniline in xylene have been studied. There was sharp increase in the separation efficiency and distribution ratio of Ce(IV), when phase ratio A/O varied from 20:1 to 3:1. The recommended procedure the phase ratio is used 2.5: 1.

Metal loading capacity of extractant

The influence of the initial Ce(IV) concentration 40-1500 µg on the extraction by *N-n*-octylaniline in xylene was studied. It was observed that, varying the initial Ce(IV) concentration in the range of 40-200 µg has no significant influence of Ce(IV) extraction with the extractant. The maximum loading capacity of 10 mL 0.13 M solution of *N-n*-octylaniline in xylene was found to be 200 µg Ce(IV).

Effect of diverse ions

The effect of various cations and anions on extraction of Ce(IV) with 0.13 M *N-n*-octylaniline in xylene was studied. The tolerance limit was set as the

amount of foreign ion causing a change $\pm 2\%$ error in the recovery of Ce(IV). Initially the foreign ion was added to the Ce(IV) solution in large excess, 100 mg for anions and 25 mg for cations. However, interference due to V(V) and Zr(IV) was eliminated by masking with 2 mg F⁻. Manganese(II) was masked with 5 mg oxalate. The ions such as EDTA, citrate interfere with the extraction of Ce(IV) by the proposed method (Table 5).

Table 5. Effect of Various Diverse Ions.

Ratio of ions Ce(IV): Ions	Tolerance limit,(mg)	Foreign ions
1:1000	50	Bromide, thiourea, salicylate, nitrate, thiosulphate
1:500	25	Malonate, acetate, iodide, nitrite
1:300	15	Oxalate, thiocyanate
1:100	5	Fluoride
1:20	1	Ascorbate
1:10	0.5	Phosphate, tartrate
1:140	7	Ca ²⁺ , Mg ²⁺
1:100	5	Sr ²⁺ , Cr ⁴⁺
1:20	1	W ⁶⁺ , U ⁶⁺ , Ni ²⁺
1:10	0.5	Cd ²⁺ , Zn ²⁺ , Re ⁷⁺ , Pd ²⁺ , Mo ⁶⁺ , Fe ²⁺ , a V ⁵⁺ , a Zr ⁴⁺ , Ba ²⁺ , Co ²⁺ , b Mn ²⁺
1:6	0.3	Sm ³⁺ , Nd ³⁺ , c Y ³⁺
1:4	0.2	Rh ³⁺ , La ³⁺ , Ti ⁴⁺

a = masked by 3 mg F⁻, b = masked by 5 mg oxalate, c = masked by 50 mg S₂O₃

Ce(IV) = 50 µg, pH = 8.5, Aq: Org ratio = 25:10, Sodium salicylate = 0.05 M, Equilibrium time = 5 min, Reagent = 10 mL 0.13 M N-*n*-octylaniline in xylene, Strippant = 2.0 M Hydrochloric acid (3 x 10 mL).

APPLICATIONS

Separation and determination of cerium(IV) from binary mixture

The separation of Ce(IV) from some commonly associated metal ions like U(VI), Th(IV), Ti(IV), Nb(V), Zr(IV), Y(III), La(III), Nd(III) and Gd(III) using N-*n*-octylaniline can be achieved by taking advantage of the difference in the extraction conditions of metal such as pH of the aqueous phase, reagent concentration and use of masking agent (Table 6).

Table 6. Separation of Ce(IV) from Binary Mixtures.

Metal ion	Metal ion added, (µg)	Average (%) Recovery*	Chromogenic ligand	Reference number
Ce (IV)	50	98.3	Arsenazo III	21
U(VI)	50	99.4	PAR	22
Ce (IV)	50	99.7		
Nb(V)	50	98.6	PAR	22
Ce (IV)	50	98.7		
Zr(IV)	150	98.9	Alizarin Red S	23
Ce (IV)	50	99.3		
Gd(III)	75	99.7	Arsenazo I	24
Ce (IV)	50	98.9		
Nd(III)	60	99.8	PAR	22
Ce (IV)	50	98.6		
Th(IV) ^a	50	99.8	Arsenazo III	25
Ce (IV)	50	99.6		
Y(III) ^b	150	99.8	Alizarin Red S	23
Ce (IV)	50	99.5		
La(III)	60	99.2	Arsenazo I	26

^a masked with 0.5 mg tartrate, ^b masked with 50 mg thiosulphate.

* Average of six determinations.

Cerium(IV) was separated from U(VI), Nb(V), Zr(IV), Gd(III) and

Nd(III) by its extraction with 10 mL 0.13 M N-*n*-octylaniline in xylene from 0.03 M sodium salicylate. Under this condition the added metal ions remained quantitatively in the aqueous phase. The aqueous phase is washed with 5 mL xylene to remove traces of the reagent. Metal ions from the aqueous phase were determined by standard methods [22-25]. Cerium(IV) from the organic phase was stripped with three 10 mL portions of 2 M hydrochloric acid and estimated as per the general procedure.

Similarly Ce(IV) was separated from Th(IV) and Y(III) by masking with 0.5 mg tartrate and 50 mg thiosulphate respectively. The masked Th(IV) and Y(III) remained in the aqueous phase quantitatively under the optimum extraction condition of Ce(IV). After demasking of Th(IV) and Y(III) with 5 mL hydrochloric acid, the solution was evaporated to dryness. They were determined spectrophotometrically with Arsenazo III at 645 nm [21] and Alizarin Red S [23], respectively.

Determination of Ce(IV) in synthetic mixture

The applicability of the method for isolation and determination of Ce(IV) in complex mixtures was studied (Table 7). In the synthetic mixtures, Ce(IV) was extracted under the optimum extraction conditions and quantitatively recovered in all mixtures.

Table 7. Separation of Ce(IV) from Synthetic Mixture.

Composition of mixture, (µg)	Average (%) Recovery*	Relative error, (%)
Ce(IV) 50; U(VI) 50; Th(IV) ^a 50	99.3	0.7
Ce(IV) 50; La(III) 60; Zr(IV) 150	99.6	0.4
Ce(IV) 50; Nb(V) 50; Zr(IV) 150	99.8	0.2
Ce(IV) 50; Y(III) ^b 150; Nb(V) 50	99.2	0.8
Ce(IV) 50; Nb(V) 50; Gd(III) 75	99.5	0.5

^a masked with 0.5 mg tartrate, ^b masked with 50 mg thiosulphate.

* Average of five determinations.

Analysis of cerium(IV) in monazite sand

About 1.0 g of monazite sand was dissolved in a mixture of nitric acid and sulphuric acid (1:1). After separating insoluble silica, the solution was diluted to 100 mL with distilled water. An aliquot of sample solution was subjected to the proposed method for the separation and determination of cerium from uranium and thorium in monazite sand. Uranium(VI) remained quantitatively in the aqueous phase. The interference of thorium(IV) was removed by masking with 0.5 mg tartrate. The amount of cerium obtained was 27.6 % against the standard value of 27.7 % Table 8.

Determination of cerium(IV) in thin film

The proposed method is also applicable for determination of Ce(IV) in thin film [CeO₂]. The amount of Ce(IV) found in the sample by the proposed method is in good agreement with amount of Ce(IV) taken in µg Table 8.

Table 8. Determination of Ce(IV) in Thin Film and Monazite Sand.

Real sample	Amount of Ce(IV) certified value	Amount found by proposed method*
Monazite sand	27.7 %	27.6 %
Thin film material	39 µg	38.70 µg

* Average of triplicate analysis

CONCLUSIONS

The proposed extractive separation method is simple, rapid, selective reproducible and suitable for separation and determination of Ce(IV) from associated metal ions and synthetic mixtures. The method is applicable to the extraction and estimation of cerium from monazite sand and semiconducting films. The extraction mechanism corresponds to an anion exchange, in which a complex of stoichiometric formula $[(RR'NH_2^+)_2[CeO(sal.)_2]^{2-}]_{org}$ is formed in the organic phase. This was determined by the conventional slope analysis method. It is free from interference of a large number of foreign ions. The solvent like xylene was non-toxic and suitable for proposed method. N-*n*-octylaniline can be synthesized at low cost, with high yield and best purity.

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