Asian Journal of Chemistry Vol. 22, No. 9 (2010), 6798-6804

A Novel Liquid-Liquid Extraction Technique for the Extraction and Separation of Yttrium(III) with Hexaacetato Calix[6]arene

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A method is proposed for the extraction of yttrium(III) using hexaacetato calix[6]arene. The optimum extraction conditions are evaluated from a critical study of the effect of pH, concentration of extractant, shaking time, concentration of various mineral acids used as stripping agents, different types of polar and non polar diluents and effect of diverse ions. Solvent extraction of yttrium(III) was carried out using hexaacetato calix[6]arene in xylene. Yttrium(III) is quantitatively extracted with 1×10^{-4} M of the ligand in xylene at pH 6 when equilibrated for 12 min. Yttrium in the organic phase was stripped with 4 M nitric acid and determined spectrophotometrically by the arsenazo(III) method at 660 nm. The metal loading capacity of the reagent is also studied. The extraction of Y(III) was carried out in the presence of various ions to ascertain the tolerance limit of individual ions. Yttrium was successfully separated from commonly associated metal ions. The method can be extended for the determination of yttrium in real samples.

Key Words: Solvent extraction, Hexaacetato calix(6)arene, Yttrium(III).

INTRODUCTION

Yttrium is an important element from an industrial point of view. Along with scandium, it is extensively used in astronavigation, electronic and metallurgical industries. Both elements are also important in nuclear energy programmes. The Finnish Chemist Johan Gadolin in a mineral found seven years earlier near Ytterby in Sweden discovered Yttrium in 1794[1]. Yttrium is associated with the heavier lanthanides[2]. Yttrium, a rare earth element has its radius similar to erbium and holmium and its chemistry is in the trivalent state[3].

Liquid-liquid extraction enjoys a favoured position among the separation techniques because of its ease, simplicity, speed and wide scope[4]. The solvent extraction separation of yttrium(III) was done using tributyl phenol[5,6], *tris*(2-ethyl hexyl)phosphate[7], *sym*-dibenzo-16-crown-5-oxyacetic acid[8] and *bis*(2-ethylhexyl) phosphoric acid[9,10]. Recently, extraction of rare earths(III) was carried out with tributyl phosphine oxide[11], with mixtures of *sec*-octylphenoxy acetic acid and

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bis(2,4,4-trimethyl pentyl)dithiophosphinic acid[12] and separation of yttrium by CA-100 using a complexing agent and from heavy lanthanides was also done[13]. Solvent extraction of yttrium with Cyanex 302 was also carried out[14].

Until now, no work has been done on the extraction and separation of yttrium(III) with hexaacetato calix[6]arene. Calixarenes are macrocyclic, oligomers that possess the capability for cationic, anionic and molecular inclusion[15]. Calixarenes as parent compounds are sparingly soluble and high melting crystalline solids. By functionally modifying either the upper and/or lower rim it is possible to prepare various derivatives with differing selectivities for various guest ions and small molecules. Calixarenes lend themselves well to many applications because of the multiplication of options for such structural elaboration[16]. Within supramolecular compounds calix[n]arene finds several advantages over crown ethers and cryptands[17]. Calixarenes modified by chemical reactions may be considered as "molecular platforms" to which functional groups are fixed. There are numerous possibilities to obtain new calixarenes. This demonstrates the wealth of class of products and the possibilities to obtain substances with interesting properties[18].

In the work done earlier, a mineral acid media was always required. During the last decade new methods were developed using other media like a salicylate media. The major advantage and novelty of this method is that a single stage highly efficient extraction procedure without the use of any media has been developed using hexaacetato calix[6]arene as an extractant. The method was also extended to separate yttrium(III) from other multicomponant mixtures.

EXPERIMENTAL

A systronics UV-visible spectrophotometer (Model No. 108) with matched 10 mm quartz cuvettes and a digital pH meter (Systronics Model No. 361) with combined glass and calomel electrodes were used.

Calix[6]arene and hexaacetato calix[6]arene were synthesized in our laboratory by the following procedure[19].

Synthesis of calix[6]arene: Calix[6]arene was prepared by dissolving about 10 g (0.666 mol) of *p-t*-butyl phenol in 6 mL of 5 M KOH and 9.70 g of a 37 % formaldehyde solution. The mixture was heated to 110-120 °C for 2 h to give a light yellow taffy like precursor. This precursor was mixed with 40 mL of xylene and heated to 210-220 °C for 3 h in the atmosphere of nitrogen with a Dean and Stark collector. The cooled reaction mixture was filtered and then suspended in 300 mL of chloroform and then shaken with 100 mL of 1 M HCl. The organic layer was separated, washed with water, dried over Na_2SO_4 and concentrated to 100 mL. The addition of methanol caused the precipitation of solid which was removed by filtration to give a colourless product. Recystallization was carried out from chloroform and methanol. The product has a melting point of 380-388 °C and yield was 80 %.

Synthesis of hexaacetato calix[6]arene: About 2 g of *t*-butyl calix[6]arene was treated with 50 mL of acetic anhydride as well as two drops of concentrated sulphuric acid. The mixture was heated and refluxed for 2 h. The crude product on recrystallization from chloroform and methanol gave white platelets with melting point of 360-362 °C and a yield of 84 %. The purity of the ligand was checked by its melting point, elemental analysis and spectral characterization. The peak at 1760 cm^{-1} is characteristic of C=O stretching (Fig. 1).

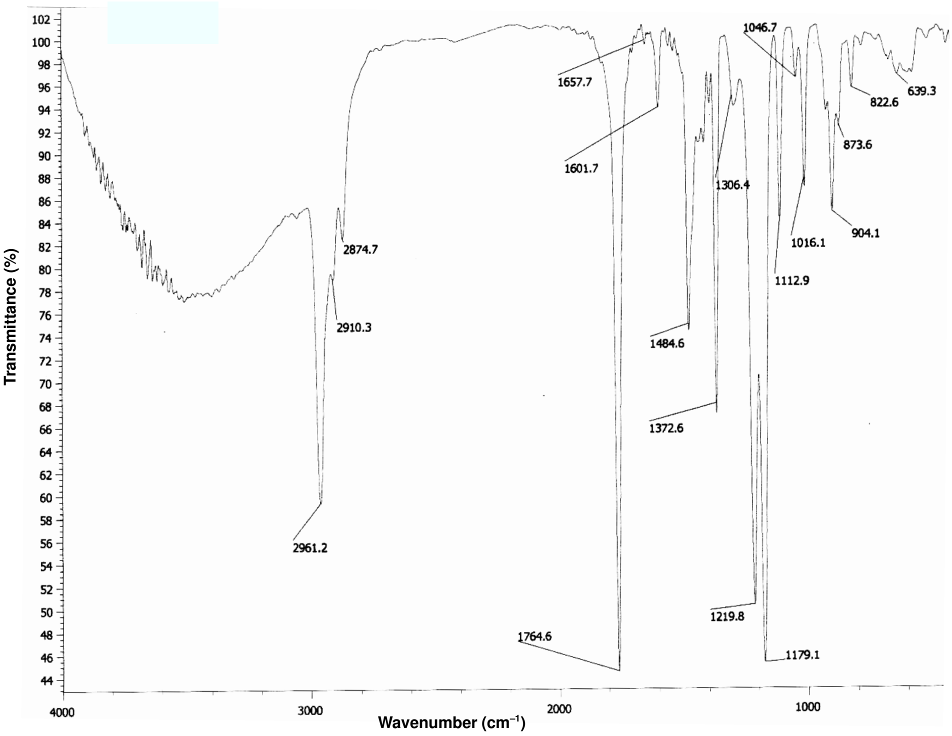


Fig. 1. IR spectral analysis of hexaacetato calix[6]arene

1 x 10^{-4} M solution of reagent was prepared in xylene. A stock solution containing 100 µg/mL of yttrium(III) was prepared by dissolving yttrium oxide in 2 % HNO_3. A diluted solution containing 5 µg/mL of yttrium(III) was prepared. 0.1 % arsenazo(III) was prepared by dissolving arsenazo(III) in distilled water.

Solvent extraction procedure: An aliquot of a solution containing yttrium(III) (5 µg/mL) was taken. It was adjusted to pH 6 with dilute HNO_3 or dilute NaOH. The total volume of the solution was made up to 10 mL with distilled water. It was then transferred to a separatory funnel. After the addition of 10 mL of 1 x 10^{-4} M of hexaacetato calix[6]arene in xylene, the solution was vigorously shaken for 12 min. The two phases were allowed to settle and separate. Yttrium(III) from the organic phase was stripped with 10 mL of 4 N nitric acid and determined spectrophotometrically at 660 nm with arsenaxo(III)[20]. The concentration of yttrium(III) was computed from the calibration curve.

RESULTS AND DISCUSSION

General extraction procedure: Yttrium(III) was extracted in the pH range of 1-9 with 1 × 10^{-4} M of hexaacetato calix[6]arene in xylene. The extraction was quantitative at pH 6 (Fig. 2).

TABLE-1
OPTIMUM EXTRACTION CONDITIONS FOR Y(III)

Metal ion	Aqueous phase pH	Organic phase	Equlibration period (min)	Stripping	Estimation procedure
Y(III)	6	10 mL of 1 × 10^{-4} M of hexaacetato calix[6]arene in xylene	12	10 mL of 4 N HNO_3	Arsenazo(III) at 660 nm

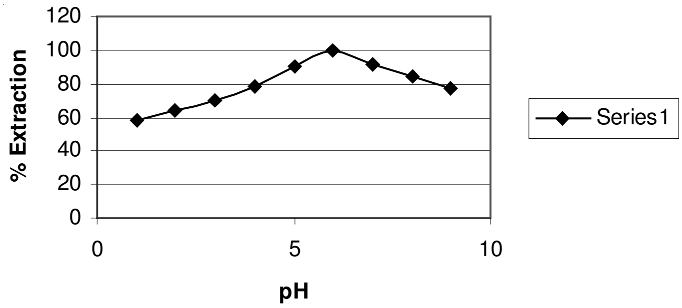


Fig. 2. Effect of pH on the extraction of yttrium(III)

Yttrium(III) was stripped quantitatively at higher concentrations of hydrochloric acid and nitric acid whereas 3 N of sulphuric acid and perchloric acid were sufficient for quantitative extraction. 4 N nitric acid was preferred as the stripping agent because of the ease in stripping. Various solvents with varying dielectric constants were used as diluents. We preferred xylene as the diluent because of its relatively less toxicity. It gave better phase separation and greater accuracy in results. It was observed that solvents having low dielectric constants show extraction of Y(III) above 90 %. When yttrium(III) was equilibrated with 1 × 10^{-4} M of hexaacetato calix[6]arene in xylene, it was observed that the extraction was quantitative for 12 min of shaking and with reagent concentration of 1 × 10^{-4} M.

Stoichiometry of the extracted species: Acetyl derivative of calixarene is a neutral extractant, capable of extracting uncharged metal complexes in aqueous solution under particular conditions and also charged metal ions and complexes. Yttrium(III) forms a stable complex with acetyl derivative of calix[6]arene in the organic phase. From the log-log plot it is found that the slope is 2 (Fig. 3). Therefore, it is concluded that the metal to ligand ratio is 1:2.

Effect of temperature and metal loading capacity: The effect of temperature was studied on the extraction of yttrium(III) from 283-353 K. It was found that the percentage of extraction increased upto 99.68 % at 303 K and thereafter remained constant until 353 K. The reaction was found to be endothermic. Yttrium(III) could be quantitatively extracted and stripped up to 50 μg/mL using 1 × 10^{-4} M of hexaacetato calix[6]arene in xylene. On increasing the concentration, extraction was not quantitative.

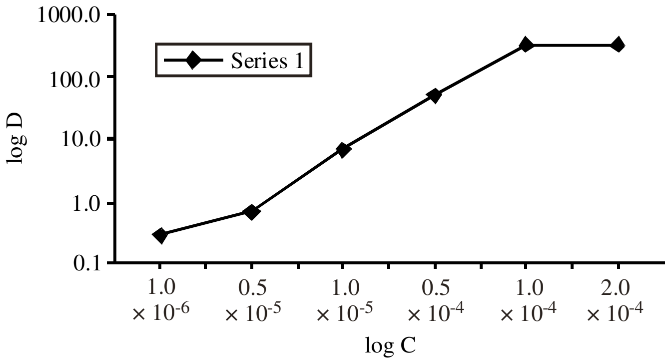


Fig. 3. Plot of log C *versus* log D

Effect of foreign ions: When Y(III) was quantitatively extracted in the presence of other metal ions, it showed a 1:20 tolerance limit for most of the I and II group elements (Table-2).

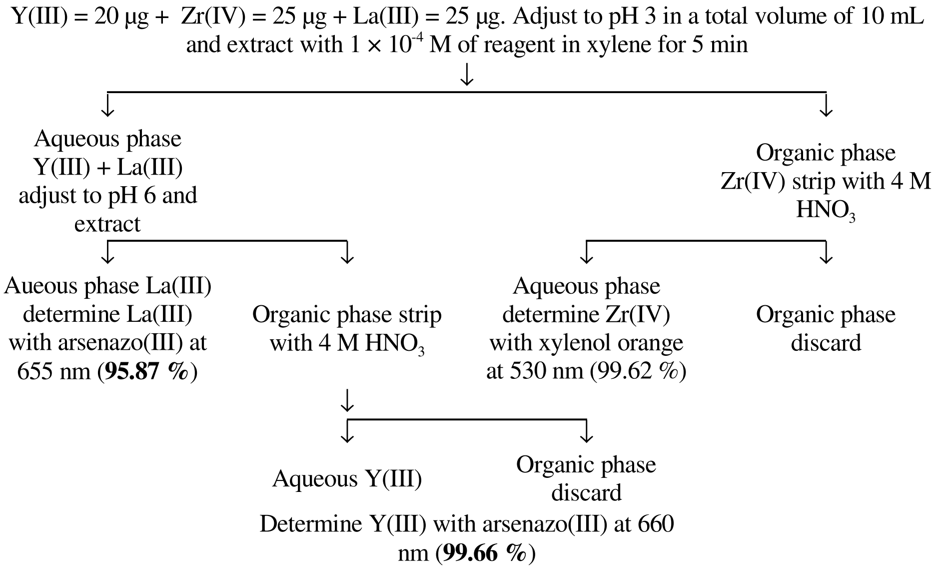
TABLE-2
EFFECT OF FOREIGN IONS ON THE EXTRACTIVE DETERMINATION OF Y(III) = 20 μg

Foreign ion	Added as	Ratio tolerated	Foreign ion	Added as	Ratio tolerated
Li^+	LiCl	1:20	Fe^{2+}	$FeCl_2$	Interfering
Na^+	NaCl	1:20	Fe^{3+}	$FeCl_3$	Interfering
K^+	KCl	1:20	Sc^{3+}	Sc_2O_3	Interfering
Mg^{2+}	$MgCl_2$	1:20	Th^{4+}	$Th(NO_3)_4$	Interfering
Co^{2+}	$CoCl_2$	1:15	Bi^{3+}	$Bi(NO_3)_3$	Interfering
Zn^{2+}	$ZnCl_2$	1:20	Pb^{2+}	$Pb(NO_3)_2$	Interfering
Mn^{2+}	$MnCl_2$	1:20	Sm^{3+}	$Sm(NO_3)_3$	Interfering
Cd^{2+}	$CdCl_2$	1:5	Cl^-	NaCl	1:20
Hg^{2+}	$HgCl_2$	1:20	F^-	NaF	1:20
Sn^{2+}	$SnCl_2$	1:20	Br^-	NaBr	1:20
Ni^{2+}	$NiCl_2$	1:15	I^-	NaI	1:20
Sr^{2+}	$SrCl_2$	1:20	CO_3^{2-}	Na_2CO_3	1:20
Ba^{2+}	$BaCl_2$	1:20	SO_3^{2-}	Na_2SO_3	1:20
V^{5+}	V_2O_5	1:20	SO_4^{2-}	Na_2SO_4	1:20
Mo^{6+}	MoO_3	1:20	PO_3^{3-}	Na_3PO_3	1:20
Cu^{2+}	$CuCl_2$	1:10	NO_2^-	$NaNO_2$	1:20
Zr^{4+}	$ZrOCl_2$	Interfering	NO_3^-	$NaNO_3$	1:20
Ca^{2+}	$CaCl_2$	1:5	Oxalate	$Na_2C_2O_4$	1:20
Cr^{3+}	$CrCl_3$	1:1	Tartarate	$Na_2C_4H_4O_6$	1:15
Al^{3+}	$AlCl_3$	1:1	EDTA	$C_{10}H_{14}O_8Na_2N_2.2H_2O$	1:10

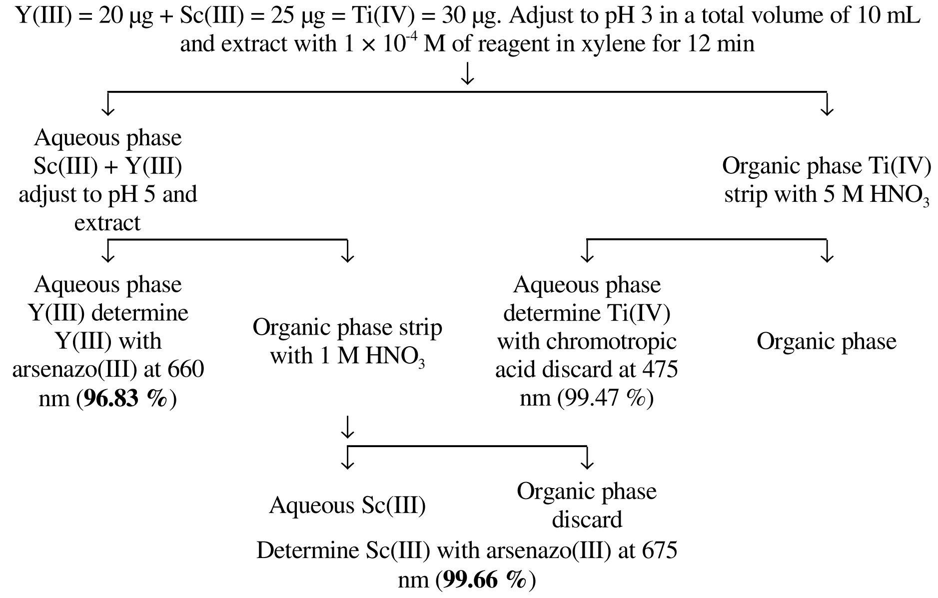
Applications

Separation of Y(III) from multi component mixtures:

Mixture 1



Mixture 2



Conclusion

The method is rapid, precise and requires a single step for completion. The method proves very useful for the separation and recovery of yttrium(III) from other synthetic mixtures and real samples.

ACKNOWLEDGEMENT

The authors are grateful to the University Grants Commission, New Delhi, India for the financial support.

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(*Received*: 1 December 2009; *Accepted*: 4 June 2010) AJC-8765