Separation of Scandium Using Liquid-Liquid Extraction with Macrocyclic Polyether(s) from Picrate Media

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Scandium was quantitatively extracted at pH 2.5—4.5 with 4.0×10^{-2} mol dm^{-3} 18-crown-6 in dichloromethane from 4.0×10^{-2} mol dm^{-3} solution of picric acid. It was stripped with 0.1 mol dm^{-3} nitric acid and determined spectrophotometrically at 650 nm as its complex with Arsenazo-III. It was separated from yttrium, lanthanides, zirconium, hafnium, vanadium, niobium, and uranium in multicomponent mixtures. Scandium from rock sample was also analysed.

Solvent extraction of scandium(III) with oxygenated solvents[1] is not quantitative, although, in the presence of salting out agent scandium can be extracted completely with tributyl phosphate.[2–5] Long chain amines were effective for its extraction.[6–7] The study of 15-crown-5, DB-18-crown 6, and DB-24-crown-8 indicated complexation is due to weak ion-dipole interaction.[8–11] However, systematic investigations on solvent extraction separation of scandium with crown ethers are lacking. Such studies are reported in this paper.

Experimental

Apparatus and Reagents: Apparatus used was similar to one described earlier.[12]

A stock solution of scandium was prepared by dissolving 0.850 g of its oxide (Merck, Germany) in 25 cm^3 of concentrated nitric acid and made upto 250 cm^3 with deionized water. The solution was standardized[13] complexometrically. It contained 2.20 mg cm^{-3} of scandium. A dilute solution containing 25 μg cm^{-3} of scandium was prepared by appropriate dilution. Picric acid (0.05 mol dm^{-3}) solution, benzo-15-crown-5 (B15C5), 12-crown-4 (12C4), 15-crown-5 (15C5), 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6), and dicyclohexyl-18-crown-6 (DC18C6) (Merck, Germany) were used without further purification.

General Procedure: To an aliquot of solution containing scandium (25 μg) picric acid was added so as to have its concentration as 4.0×10^{-2} mol dm^{-3} in total volume of 10 cm^3. Then pH of the solution was adjusted to 2.5—4.5 with 0.05 mol dm^{-3} picric acid or lithium hydroxide solution. The solution was transferred to a separatory funnel and 10 ml of 4.0×10^{-2} mol dm^{-3} of 18C6 in dichloromethane was added to it and it was shaken on wrist action shaker for 10 min. The two phases were allowed to settle and separate. Scandium from the organic phase was stripped with 0.1 mol dm^{-3} nitric acid and it was determined spectrophotometrically as its complex with Arsenazo-III.[14] The concentration of scandium was calculated from the calibration curve.

Results and Discussion

Extraction as the Function of pH: Scandium was extracted at different pH to ascertain optimum pH for quantitative extraction. The phase volume ratio was maintained as 1 : 1. The extraction commenced at pH 1.5 and was complete at pH 2.5—4.5 only with 18C6. With other extractants it was not quantitative. Hence, 18C6 was used in subsequent studies (Fig. 1).

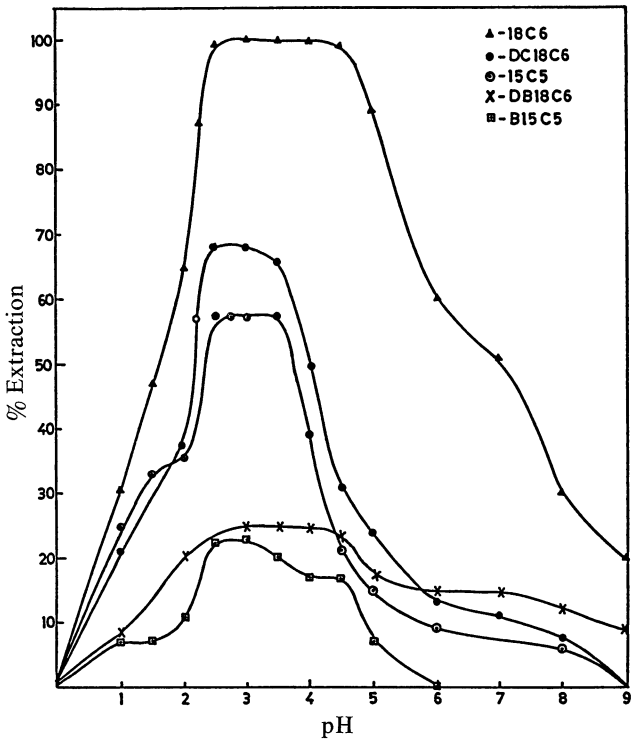

Fig. 1. Extraction of the scandium as the function of pH.

Extraction as the Function of 18C6 Concentration: Scandium was extracted at pH 2.5—4.5 with varying concentration of crown ether in dichloromethane (Table 1). The extraction was incomplete below 3.5×10^{-2} mol dm^{-3} 18C6 while it was quantitative with 4.0×10^{-2}

Table 1. Effect of 18-Crown-6 Concentration on Extraction of Scandium(III)

[18C6]/10^{-2} mol dm^{-3}	% E	D
0.5	9.1	0.10
1.0	32.0	0.47
1.5	50.3	1.01
2.0	64.2	1.79
2.5	75.0	3.0
3.0	88.0	7.33
3.5	95.0	19.0
4.0—10	>99.9	999

Table 2. Effect of Picric Acid Concentration on Extraction of Scandium(III)

[Picric acid]/10^{-2} mol dm^{-3}	% E	D
0.5	5.0	0.05
0.70	15.2	0.17
1.5	33.2	0.49
2.0	55.0	1.22
3.0	81.0	4.26
3.3	90.2	9.2
3.8—5.0	99.9	999

mol dm^{-3} 18C6 in dichloromethane.

Extraction as the Function of Picric Acid Concentration: Among the various counter ions such as eosin, tropeolin 00, dipicrylamine, Metanil Yellow, and picric acid, only picric acid was most suitable as it was capable of forming stable ion pair complex. Scandium was extracted with various concentrations of picric acid in concentration range of 0.5×10^{-2}—5.0×10^{-2} mol dm^{-3}. The extraction was quantitative above 4.0×10^{-2} mol dm^{-3} picric acid (Table 2).

Effect of on Diluent on Extraction: Benzene, toluene, xylene, carbon tetrachloride, chloroform, dichloromethane, dichloroethane, nitrobenzene, and cyclohexane were tested as the diluents (Table 3). Dichloromethane, dichloroethane, and nitrobenzene were effective as the diluents whereas all other diluents showed incomplete extraction.

Effect of Stripping Agents: Scandium was stripped with hydrochloric, nitric, sulfuric, perchloric, and acetic acid. Hydrochloric and acetic acid were effective from 2.0—7.0 mol dm^{-3} while other stripping agents were good from 0.1—0.7 mol dm^{-3}. 0.1 mol dm^{-3} nitric acid was used as the stripping agent in this work (Table 4).

Table 3. Effect of Diluents

Solvents	Dielectric constant E	% E	D
Cyclohexane	2.0	87.0	6.69
Benzene	2.28	17.5	0.21
Toluene	2.30	8.7	0.10
Xylene	2.38	5.6	0.06
Carbon tetrachloride	2.24	21.0	0.265
Chloroform	5.8	89.1	8.17
Dichloromethane	9.08	100.0	∞
Dichloroethane	10.5	100.0	∞
Nitrobenzene	34.8	100.0	∞

Table 4. Effect of Stripping Agents[a)]

Stripping agent	Scandium stripped/%				
	0.01 M	0.025 M	0.05 M	0.1 M	2—7 M
HCl	17.0	31.0	47.3	82.1	100
HNO_3	21.0	52.1	83.1	100	100
H_2SO_4	27.0	47.3	81.2	100	100
$HClO_4$	30.9	59.0	76.1	100	100
CH_3COOH	23.1	37.0	53.0	76.1	100

a) 1 M=1 mol dm^{-3}.

Effect of Shaking Period on Extraction: The extraction was carried out for various time of shaking from 2 to 20 min. Beyond 8 min shaking the extraction attained equilibrium. In order to ensure complete extraction 10 min shaking was employed.

Nature of Extracted Species: The composition of extracted species was ascertained by plotting a log D vs. log[18C6] at fixed picric acid concentration and a graph of log D vs. log[picric acid] at fixed 18C6 concentration. The corresponding slopes were 1.96 and 2.87 respectively. Hence the probable composition of extracted species was scandium : 18C6 : picric acid=1 : 2 : 3 i.e. $[Sc(pic)_3\cdot(18C6)_2]$. These findings were in agreement with those of earlier workers.[10)]

Separation from Binary Mixtures: Scandium was extracted in the presence of several ions. The tolerance limit was set as the amount of foreign ion and not salt which is causing an error of less than ±0.5% in the recovery of scandium. Since pH for extraction of scandium and alkali metals are different under condition of extraction of scandium, alkali and alkaline earths are not extracted. Alkali and alkaline earths were tolerated in the ratio of 1 : 6 to 1 : 80 except lithium tolerated in the ratio of 1 : 200. Yttrium, titanium, zirconium, hafnium, and uranium were tolerated in the ratio of 1 : 40 while thorium was tolerated in the ratio of 1 : 4.

Table 5. Separation of Scandium from Binary Mixtures Sc=25 μg, picric acid=4.0×10^{-2} M, 18C6=4.0×10^{-2} M, pH=2.5

Foreign ions	Added as	Tolerance limit/μg
Li(I)	LiCl	5000
Na(I)	NaCl	300
K(I)	KCl	150
Cs(I)	CsCl	300
Be(II)	$BeCl_2$	2000
Mg(II)	$MgSO_4\cdot7H_2O$	1500
Ca(II)	$CaCl_2\cdot6H_2O$	1000
Sr(II)	$Sr(NO_3)_2\cdot2H_2O$	500
Ba(II)	$Ba(NO_3)_2\cdot4H_2O$	300
Y(II)	$Y(NO_3)_3$	1000
Ti(IV)	$Ti(SO_4)_2$	1000
ZrO(II)	$Zr(NO_3)_4\cdot4H_2O$	1000
HfO(II)	$Hf(SO_4)_2\cdot4H_2O$	1200
Th(IV)	$Th(NO_3)_4\cdot6H_2O$	100
UO_2(II)	$UO(NO_3)_2\cdot6H_2O$	800
VO(II)	$VOSO_4\cdot H_2O$	1500
Nb(V)	Nb_2O_5	900
Cr(III)	$Cr(NO_3)_3$	900
Mo(VI)	$(NH_4)_2MoO_4\cdot4H_2O$	1000
Mn(II)	$MnSO_4\cdot4H_2O$	700
Fe(III)	$FeCl_3$	1500
Co(II)	$Co(NO_3)_2\cdot6H_2O$	1200
Ni(II)	$NiSO_4\cdot6H_2O$	900
Zn(II)	$ZnSO_4\cdot7H_2O$	1000
Cd(II)	$3CdSO_4\cdot8H_2O$	1200
Cl^-	LiCl	5000
NO_3^-	$LiNO_3$	4000
ClO_4^-	$HClO_4$	4000
Acetate	CH_3COOH	3500

The common anions were tolerated in the ratio of 1 : 200 (Table 5).

Separation from Multicomponent Mixtures: A mixture of scandium, cerium(III), and yttrium was separated by first extracting scandium with 4.0×10^{-2} mol dm^{-3} 18C6 from 4.0×10^{-2} mol dm^{-3} picric acid at pH 2.5. Then cerium(III) was extracted with 5.0×10^{-2} mol dm^{-3} 15C5 at pH 6.0. Scandium and cerium were stripped with 0.1 mol dm^{-3} nitric acid and 1 mol dm^{-3} perchloric acid respectively. Since yttrium was not extracted, it was determined directly from the aqueous phase. Since size of the hydrated scandium species is large, it readily reacts with 18-crown-6 to form complex in comparison with that of yttrium in the presence of picrate anion.

Scandium was separated from mixture of scandium, lanthanum, and yttrium by extracting it with 4.0×10^{-2} mol dm^{-3} 18C6 followed by extraction of lanthanum at pH 4.5 with 1.0×10^{-1} mol dm^{-3} 18C6 from 4.0×10^{-2} mol dm^{-3} picric acid. Since yttrium was not extracted, it was determined directly from the aqueous phase.

A mixture of lead, scandium, and aluminium was resolved by first extracting lead with 2.0×10^{-2} mol dm^{-3} DB18C6 at pH 3.0 from 1.0×10^{-2} mol dm^{-3} picric acid followed by extraction of scandium with 4.0×10^{-2} mol dm^{-3} 18C6 from 4.0×10^{-2} mol dm^{-3} picric acid when aluminium was not extracted and it remained unextracted in the aqueous phase.

A mixture of scandium, iron(III), zirconium, and titanium was separated by first extracting scandium with 4.0×10^{-2} mol dm^{-3} 18C6 from 4.0×10^{-2} mol dm^{-3} picric acid. Iron(III) was latter extracted with 1.0×10^{-2} mol dm^{-3} DB18C6 from 7.0 mol dm^{-3} hydrochloric acid followed by extraction of zirconium with 2.5×10^{-2} mol dm^{-3} DC18C6 from 8.5 mol dm^{-3} hydrochloric acid. Titanium remained in the aqueous phase as unextracted species.

Similarly scandium was separated from niobium(V)/uranium(VI), hafnium, and vanadium(IV) by extracting first scandium with 4.0×10^{-2} mol dm^{-3} 18C6 from 4.0×10^{-2} mol dm^{-3} picric acid. The niobium/uranium was extracted with 2.0×10^{-2} mol dm^{-3} DC18C6 from 7.0 mol dm^{-3} hydrochloric acid, finally, hafnium was extracted with 7.0×10^{-2} mol dm^{-3} DC18C6 from 9.0 mol dm^{-3} hydrochloric acid. The unextracted vanadium remained in the aqueous phase (Table 6).

Analysis of Scandium from Real Samples: About 0.5 g of rock sample was dissolved in a mixture of hydrofluoric and nitric acid (1 : 1) and was evaporated to dryness. The solution after filtration was diluted to 250 ml. An aliquat of solution containing barium, iron, zirconium, hafnium, yttrium, vanadium and aluminium was taken and first barium was extracted with 1.0×10^{-2} mol dm^{-3} DB18C8 in nitrobenzene from 1.0×10^{-2} mol dm^{-3} picric acid at pH 6.0 then scandium was extracted with 4.0×10^{-2} mol dm^{-3} 18C6 from 4.0×10^{-2} mol dm^{-3} picric acid at pH 2.5. From the organic phase scandium was stripped with 0.1 mol dm^{-3} nitric acid and determined spectrophotometrically. All other elements did not interfere during the extraction of scandium. The amount of scandium in the rock sample was 3.43% against the standard value of 3.5% which was determined by atomic absorption spectrometer.

The proposed method is simple, rapid, and selective. The total time required for extractive separation and determination is about 2 h. The relative standard deviation was ±1.9%. The separation of scandium from yttrium, lanthanum, cerium, uranium, zirconium, hafnium, and niobium was significant.

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Table 6. Separation of Scandium from Multicomponent Mixtures

Sr. No.	Mixture	Extractant	Counter anion	pH	Amount taken (μg)	% Recovery	Stripping agent
1	Sc	0.04 M 18C6	0.04 M Picrate	2.5	25	99.7	0.1 M HNO_3
	Ce(III)	0.05 M 15C5	0.04 M Picrate	6.0	15	99.0	1.0 M $HClO_4$
	Y	Unextracted	—	—	50	100	Aq phase
2	Sc	0.04 M 18C6	0.04 M Picrate	2.5	25	99.1	0.1 M HNO_3
	La(III)	0.1 M 18C6	0.04 M Picrate	4.5	25	97.6	0.05 M H_2SO_4
	Y	Unextracted	—	—	50	99.8	Aq phase
3	Pb(II)	0.02 M DB18C6	0.01 M Picrate	3.0	25	99.7	1.0 M $HClO_4$
	Sc	0.04 M 18C6	0.04 M Picrate	2.5	25	99.0	0.1 M HNO_3
	Al	Unextracted	—	—	50	99.8	Aq phase
4	Sc	0.04 M 18C6	0.04 M Picrate	2.5	25	99.0	0.1 M HNO_3
	Fe(III)	0.01 M DB18C6	7.0 M Chloride	—	50	99.7	0.5 M H_2SO_4
	Zr(IV)	0.025 M DC18C6	8.5 M Chloride	—	25	99.1	0.5 M HCl
	Ti(IV)	Unextracted	—	—	50	99.7	Aq phase
5	Sc	0.04 M 18C6	0.04 M Picrate	2.5	25	99.6	0.1 M HNO_3
	Nb/UO_2(II)	0.02 M DC18C6	7.0 M Chloride	—	25	99.1	0.5 M HCl
	Hf(IV)	0.07 M DC18C6	9.0 M Chloride	—	25	98.7	0.1 M $HClO_4$
	V(IV)	Unextracted	—	—	50	100	Aq phase

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