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Liquid-Liquid Extraction and Separation of Lanthanum (III)

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Separation of lanthanum(III) from iron(III), molybdenum(VI), vanadium(V), chromium(VI), titanium (IV), bismuth(III), zirconium(IV), scandium(III), uranium(VI), and beryllium is achieved by solvent extraction with mesityl oxide from sodium salicylate solution (0.1 M adjusted to pH 7). Lanthanum from the organic phase is stripped with water and determined photometrically as its arsenazo complex at 570 nm. The extracted species is trisolvated *i.e.* $La(HOC_6H_4COO)_3 \cdot 3MeO$. The results of separation are reported.

Mesityl oxide has been used in this laboratory for the solvent extraction of uranium from salicylate media.[1] In this communication we propose a simple and rapid method for the selective extraction of lanthanum from 0.1 M sodium salicylate solution (adjusted to pH 7) into mesityl oxide. The lanthanum (III) from the organic phase is stripped with water and determined photometrically with arsenazo[2] at 570 nm. The method affords separation of lanthanum from iron (III), molybdenum(VI), vanadium(V), chromium(VI), titanium(IV), bismuth(III), zirconium (IV), scandium(III), uranium(VI), and beryllium.

Extraction of lanthanum with various chelating agents have been reviewed by Stary in his monograph.[3] The extraction of lanthanum from nitric acid, perchloric acid or thiocyanate media with oxygen containing solvents, organophosphorus acids, esters and oxides have been earlier reported.[4—17] Extraction with high molecular weight amines and carboxylic acids have also been reported,[18—20] but systematic separation studies of lanthanum is lacking. This communication describes a simple and rapid method for the solvent extraction of lanthanum(III) from sodium salicylate solution (pH 7) using mesityl oxide as an extractant. The method permits selective separation of lanthanum from metal ions such as iron, molybdenum, vanadium, chromium, titanium, zirconium, bismuth, scandium, uranium, and beryllium.

Experimental

Apparatus and Reagents. Absorbances were measured with a Zeiss Spectrophotometer (Jena) employing 1 cm quartz cells and pH values were measured with Philips pH meter (Precision type).

The stock solution of lanthanum was prepared by dissolving 0.587 g of lanthanum(III) oxide (BDH, England) in 4 ml of concentrated hydrochloric acid and diluting to 100 ml with distilled water. The solution was standardized by known method[21] and further diluted as required for working solutions.

Mesityl oxide, bp 125—128 °C (BDH) was used after double distillation.

Arsenazo I, 0.05% aqueous solution was used.

All other chemicals used in this work were of guaranteed grade.

General Extraction Procedure. Take an aliquot solution containing 40 μg of lanthanum, add sodium salicylate (0.4 g) to give the final concentration of 0.1 M in a total volume of 25 ml. Adjust the pH of the solution to 7 by diluted NaOH/HCl solutions and transfer into a 100 ml separatory funnel. Equilibrate the mixture for 30 s with 10 ml of neat mesityl oxide. Allow the layers to settle and strip lanthanum from organic phase with two 10 ml portions of water (containing a few drops of HCl to avoid emulsion) and determine it photometrically with arsenazo I at 570 nm.

Results and Discussion

Effect of pH, Salicylate Concentration and Mesityl Oxide Concentration. The extraction of lanthanum was studied at various pH. The extraction commences at pH 3, becomes quantitative at pH 7 and then decreases (Fig. 1). The pH was adjusted with diluted NaOH/HCl solutions. The optimum pH for quantitative extraction of lanthanum is 7. The concentration of mesityl oxide was varied from 35 to 100% with benzene as diluent and the sodium salicylate concentration was varied from 0.01 to 0.1 M. The results show that lanthanum extracts quantitatively from 0.1 M sodium salicylate solution with neat mesityl oxide. The percentage extraction of the metal ions was computed by stripping the metal ion from the organic phase and subsequent photometric determination with arsenazo I. The distribution ratio was calculated by using relationship.

$$\%E = \frac{100D}{D(V_w/V_o)}$$

where V_w and V_o are the volumes of aqueous and organic phase respectively. A log-log plot of distribution ratio *vs.* mesityl oxide concentration at fixed

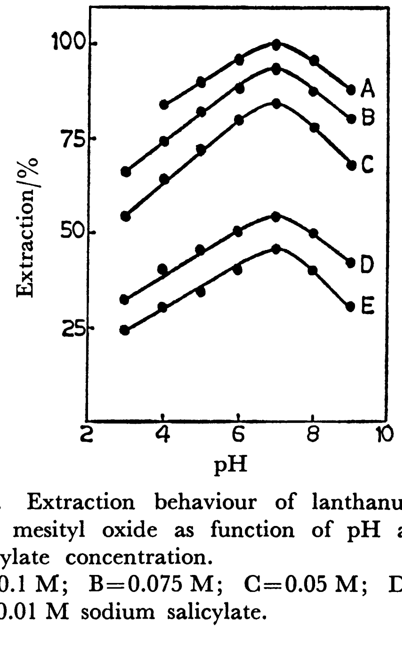
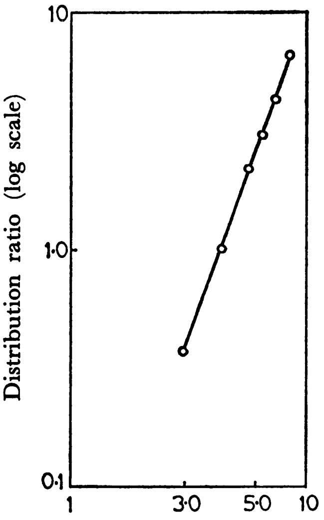
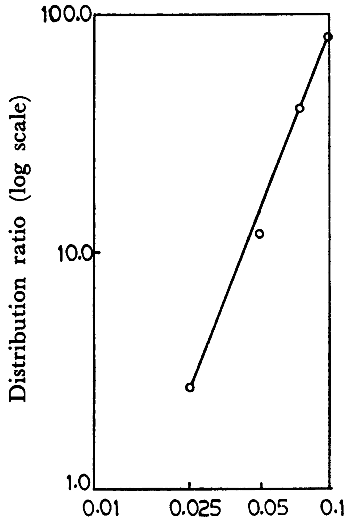


Fig. 1. Extraction behaviour of lanthanum-salicylate into mesityl oxide as function of pH and sodium salicylate concentration.
A=0.1 M; B=0.075 M; C=0.05 M; D=0.025 M; E=0.01 M sodium salicylate.



Concentration of mesityl oxide (log scale)

Fig. 2. Distribution ratio of lanthanum as a function of mesityl oxide concentration at 0.05 M sodium salicylate concentration and pH 7.



Concentration of mesityl oxide (log scale)

Fig. 3. Distribution ratio of lanthanum as a function of sodium salicylate concentration at pH 6.5

pH (7.0) and salicylate concentration (0.05 M) gave a slope of 2.7 (Fig. 2) indicating the presence of three solvent molecules in the extracted species. Similarly the log-log plot (Fig. 3) of distribution ratio *vs.* salicylate concentration at fixed pH (6.5) and mesityl oxide concentration gave a slope of 2.6 indicating a molar ratio of 1:3 for the reaction of lanthanum and salicylate ion. The extraction equilibria for lanthanum (III) extraction (from salicylate media) into mesityl oxide could be written as:

$$La^{3+} + 3(HOC_6H_4COO)^- \rightleftharpoons La(HOC_6H_4COO)_3 \quad (1)$$

$$La(HOC_6H_4COO)_3 \cdot 3\,H_2O + 3\,MeO \rightleftharpoons La(HOC_6H_4COO)_3 \cdot 3\,MeO + 3\,H_2O. \quad (2)$$

MeO stands for mesityl oxide.

The extractable species is thus trisolvated.

Distribution of Salicylic Acid and Sodium Salicylate.

Table 1. Distribution ratio of salicylic acid (A) and sodium salicylate (B) between mesityl oxide and aqueous solution

$\mu = 0.1$ M sodium perchlorate

	pH[a]	D_{Sal} (Exptl)	$D_{Sal}\left(1+\frac{K_1}{[H^+]}\right)$	D_{Sal} (Calcd)
(A)	4.5	2.86	115.7	2.03
	5.5	2.33	177.4	0.30
	6.5	2.16	768.1	0.13
(B)	5	0.31	129.5	0.72
	6	0.19	311.4	0.17
	7	0.11	2122.0	0.12

a) Before extraction.

The distribution of salicylic acid and sodium salicylate between mesityl oxide and aqueous solution of different pH values (adjusted with diluted perchloric acid and sodium hydroxide solution) at constant ionic strength (0.1 M sodium perchlorate) was studied by equilibrating known concentration of salicylic acid or sodium salicylate for more than 16 hours at room temperature. The volume of aqueous phase and organic phase was kept equal (10 ml). After equilibration the layers were allowed to settle and separate and concentration of unextracted salicylic acid or salicylate ions in the aqueous phase is determined colorimetrically. The experimental distribution ratio and the calculated one are obtained by equations given by Irwing and Sinha[22] and reported in Table 1. Both salicylic acid and sodium salicylate show extraction into mesityl oxide but the probability of dimerization of salicylic acid in mesityl oxide which is a ketone is negligible.

The period of equilibration was varied and for quantitative extraction of lanthanum, single extraction for 30 s with neat mesityl oxide is adequate. Prolonged shaking has no adverse effect on the extraction.

An interference study showed that for the extraction of 40 μg of lanthanum by the recommended procedure, 2500 μg each of Ag, Ca, Ba, Zn, Hg, Ni, Bi, As(III), Au(III), Ti(IV), Zr(IV), Ga(III), Mo(VI), tartrate, ascorbate, nitrate, thiocyanate, sulfate, thiourea, phosphate and carbonate do not interfere. Similarly no interference is observed for 2000 μg each of Co, Mn, Fe(III); 1000 μg each of Pd, Cd, Pb, V(V), Cr(VI), fluoride; 500 μg each of Sn(II), Al, Rh, Ru, W(VI), and 100 μg of Cr(III). However, cerium (III and IV) and Nd(III) interfere severely.

Separation of Lanthanum(III) from Iron(III), Molybdenum(VI), Vanadium(V), Chromium(VI), Titanium(IV), and Beryllium. Ions such as iron, molybdenum, vanadium(V), chromium(VI), beryllium, and titanium(IV) do not extract into mesityl oxide. Hence their separation (from binary mixtures) is achieved by extraction of lanthanum by the recommended procedure. Lanthanum from the organic phase is stripped and determined as described above and the added ions, are estimated in the aqueous phase by standard procedure. The recovery of lanthanum and added

TABLE 2. ANALYSIS OF SYNTHETIC MIXTURES

Sample No.	Composition of synthetic mixture and amount taken in mg	Recovery of Lanthanum from duplicate analysis %	Relative error %	Recovery of added ion %	Relative error %	Estimation procedure for added ions and references
1	La, 0.04; Fe, 1.0	99.8	0.2	99.6	0.4	Colorimetry with thiocyanate (23)
2	La, 0.04; Mo, 2.5	99.8	0.2	99.6	0.4	Colorimetry with thiocyanate (23)
3	La, 0.04; V, 0.5	99.6	0.4	99.2	0.8	Colorimetry with PAR (24)
4	La, 0.04; Cr, 1.5	99.4	0.6	99.4	0.6	Colorimetry with diphenylcarbazide (23)
5	La, 0.04; Ti, 1.0	99.6	0.4	99.0	1.0	Colorimetry with H_2O_2 (23)
6	La, 0.04; Zr, 2.5	99.2	0.8	99.0	1.0	Complexometry with EDTA (25)
7	La, 0.04; Bi, 1.0	99.4	0.6	99.2	0.8	Colorimetry with thiourea (23)
8	La, 0.04; Sc, 0.025	99.0	1.0	99.0	1.0	Colorimetry with arsenazo I (26)
9	La, 0.04; U, 0.5	99.2	0.8	99.2	0.8	Colorimetry with PAR (27)
10	La, 0.04; Be, 1.0	99.2	0.8	99.0	1.0	Colorimetry with aluminon (28)

Note: (1) Lanthanum is estimated photometrically with arsenazo I. (2) Aqueous solution containing titanium, scandium, or beryllium is evaporated to dryness, treated with HNO_3 and $HClO_4$ to decompose salicylate and residue is dissolved in water and then used for titanium or scandium or beryllium estimation.

ions is >99.0%. The results of the analysis of synthetic mixtures are reported in Table 2.

Separation of Lanthanum from Zirconium(IV) and Bismuth(III) Both zirconium and bismuth show coextraction with lanthanum, but do not back extract with water. Separation of lanthanum from binary mixture is achieved by first stripping lanthanum with water and subsequent scrubbing of zirconium with two 10 ml portions of 1 M HCl solution and bismuth with two 10 ml portions of 1 M NaOH solution. The results of the separation are reported in Table 2.

Separation of Lanthanum(III) from Scandium(III) and Uranium(VI). Lanthanum (from 0.1 M sodium salicylate solution adjusted to pH 7) also extracts into 4-methyl-2-pentanol but scandium and uranium do not. This facilitates separation of lanthanum from scandium and uranium. Binary mixture containing lanthanum–scandium or lanthanum–uranium in 0.1 M sodium salicylate solution adjusted to pH 7, is extracted for 30 sec with 10 ml of undiluted 4-methyl-2-pentanol. Lanthanum transfers into organic phase keeping scandium and uranium in the aqueous phase. Lanthanum is stripped with two 10 ml portions of water containing few drops of HCl and then determined as described above. Scandium and uranium in the aqueous extract are estimated by known methods. Separation results are reported in Table 2.

The reproducibility of results was satisfactory and results were found to be accurate within ±0.5% with the standard deviation of ±0.8%. The total operation requires only 15 min. The wide applicability of the method is shown by the satisfactory analysis of a variety of samples.

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