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ORIGINAL ARTICLE

Liquid–liquid anion exchange extraction studies of samarium(III) from salicylate media using high molecular weight amine

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Synthetic mixtures

Abstract Liquid–liquid extraction and separation of samarium(III) was carried out by using 0.025 mol dm^{-3} 2-octylaminopyridine(2-OAP) in xylene at 298 K. The extraction behavior of samarium was studied as a function of pH, weak acid concentration, extractant concentration, diluent, and equilibration time. Samarium was quantitatively extracted at pH 7.5 to 10.0 from 0.01 mol dm^{-3} sodium salicylate solution with 0.025 mol dm^{-3} 2-OAP. The possible composition of the extracted species in organic phase has been determined by using model of slope analysis method and extraction mechanism was found to proceed via an anion exchange mechanism. The stripping efficiency was found to be quantitative in HNO_3, HCl and CH_3COOH. The robustness of the procedure was demonstrated by the average recoveries obtained (>99.6%) for samarium(III) extraction in the presence of several cations and anions which are commonly associated with it. The proposed method facilitates the separation and determination of samarium(III) from binary and synthetic mixtures. The various thermodynamic functions like free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of extraction mechanism were discussed.

1. Introduction

Intricately similar in their chemical properties, lanthanides pose an exigent problem in their separation. Therefore, separation of trivalent lanthanides is still a very important and serious problem. Among the different methods used for this purpose, solvent extraction is one of the most popular and versatile technique. The separation of rare-earth elements by solvent extraction is an interesting subject to attract a number of researchers (Scargill et al., 1957; Pierce and Peck, 1963). The

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use of these ions in technical and medical field is growing annually. For a variety of uses in various important fields such as magnetism, metallurgy and phosphors, catalysts, glass and ceramic technology, high purity of metals is often required (Sabot et al., 1996). The interest concerning rare earths in the international market is due to the widespread use of these elements, which in a high purity isolated form may cost several times more than in a mixed state (O'Driscoil, 1988). The development of the samarium–cobalt permanent magnet, with flux densities for higher than that of current similar products has turned samarium(III) into an industrial material of outstanding significance. In view of these facts, preconcentration and separation of rare earth's like samarium(III) at trace levels has received considerable attention for ease of manipulation and routine operation.

The extractive separation of samarium(III) from nitrate solution by some phosphine oxide compounds such as cyanex 921, 923 and 925 (El-Nadi et al., 2007) in kerosene was investigated. Separation of samarium(III) was carried out by using extractants 2-ethylhexylphosphonic acid, mono-2-ethylhexyl ester diluted in isododecane from gadolinium(III) in monazite sand (Miranda and Zinner, 1997). A batch and continuous scale study has been carried out with phosphoric acid (D2EHPA), phosphonic acid (IONQUEST 801) and a phosphinic acid (Cyanex 272) for the extractive separation of samarium from gadolinium (Benedetto et al., 1993). A distribution of trivalent samarium(III) between hydrochloric acid solution and solutions of di-(2-ethylhexyl)-phosphoric acid (DEHPA) or 2-ethylhexyl 2-ethylphosphonic acid (EHEHPA) in kerosene with 10 min shaking has been investigated (Sato, 1989). A batch process was developed to separate the samarium from monazite mineral of the Egyptian beach black sand deposits after cerium separation. The process was based on extraction by di-2-ethylhexyl phosphoric acid/kerosene from nitric–hydrochloric acid mixture (Rabie, 2007). However, in these methods, stripping requires many contacts with the organic phase for recovery of the metal. In general the extraction by phosphoric acid extractants were strongly affected by their extractability being insufficient and their low loading capacity for samarium(III) results from the low lipophilicity of coordination compounds form during the extraction.

As a branch of solvent extraction, synergistic extraction has become a common method for the separation of metal ions. It not only improve the extraction efficiency but also improves the extraction selectivity and also enhance the stability of the extracted complexes, improve the stability of extracted complexes in the organic phase, eliminate the emulsification and the formation of the third phase and increase the extraction rate (Mathur, 1983). Mixture of chelating agent and neutral donor has been extensively used in the synergistic extraction of trivalent samarium. The methods devoted to synergistic extraction of samarium contains organophosphoric compounds like dibutylmonothiophosphoric acid (DBTPA) and dibutyl phosphoric acid (DBPA) as extractant and tri-*n*-butylphosphine oxide (TBPO), dibutylphosphate (DBOBPO) and tri-*n*-butylphosphate (TBOPO) as synergist (Kondo et al., 2009), dibutylmonothiophosphoric acid and 1–10 phenanthroline (Kondo et al., 1990), di(2-ethylhexyl)phosphoric acid and 1–10 phenanthroline (Zahir and Masuda, 1997) sec-octylphenoxy acetic acid, bis (2,4,4-trimethylpentyl) dithiophosphinic acid (Jia et al., 2009), sec-nonylphenoxy acetic acid and 1–10 phenanthroline (Fan et al., 2010). The extraction of samarium(III) has been systematically carried out by using synergistic extraction with calix[4]arene carboxylic derivative and primary amine N1923 (He et al., 2008), *n*-*p*-methoxybenzoyl-*n*-phenylhydroxylamine and neutral nitrogen donors (Inoue et al., 2007), 4-benzoyl-3-methyl-1-phenyl-2-pyrazoline-5-one and aliquat 336 (Atanassova and Dukov, 2004).

Recently, amides in the organic diluents have been found to be efficient extractants for actinides and lanthanides in the coextraction and separation of transplutonium and trivalent lanthanides (Mowafy and Aly, 2002; Sasaki and Tachimor, 2002; Cuillerdier et al., 1991; Sun et al., 2002). A study has been made for the extraction of samarium(III) from nitrate solution, using *N*,*N*,*N*′,*N*′-tetrabutylmalonamide [TBMA] in series of diluent, extraction was dependent on diluent used (Guo-Xin et al., 2004). *N*,*N*-Dimethyl-*N*′*N*′-diphenylpyridine-2,6-dicarboxyamide (DMDPhPDA) was used as an extractant for samarium(III) from 1 to 5 mol dm^{-3} nitric acid solution. The extraction of samarium(III) is sensitive toward nitric acid concentration (Shimada et al., 2004). Picrolonic acid in MIBK has been used for the extraction of samarium(III) from pH 1 to 2. However, among the various anions, fluoride, oxalate and cyanide ions and among the cations Zn(II), Cu(II), Co(II) and Fe(III) reduced the lanthanide extraction (Ali and Ahmed, 2005). The solvent extraction behavior of samarium(III) has been investigated using 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone as an extractant in aqueous benzene medium. The extraction procedure needs 60 min shaking at room temperature to attain equilibrium and benzene was used as toxic solvent (Jordanov et al., 2002).

There are very few research papers reported for extractive separation of samarium(III) using high molecular weight amines. Tri-*n*-octylamine [TOA] in benzene was used for extraction of samarium(III) from succinate media in the pH range 6.5–7.5. This method requires higher reagent concentration in toxic solvent like benzene (Desaiand Shinde, 1985). The extraction separation of samarium(III) by benzyldibutyl amine [BDBA] (Kovalancik and Galova, 1992) from aqueous nitrate solution was not found very efficient but it could remarkably improves extraction by addition of complexing agent such as EDTA.

In this study, the solvent extraction of samarium(III) was investigated in order to elucidate the extraction mechanism. The optimized extraction conditions of samarium(III), the extraction mechanism, effect of various anions and cations on their extraction and their separation from various associated metal ions are also presented. The method is found to be eco-friendly as the extraction is carried out from weak organic acid media and use of less toxic solvent like xylene through out the study.

2. Experimental

2.1. Apparatus

An Elico digital spectrophotometer Model SL-171 MINI SPECTRO with 1 cm quartz cells was used for absorbance measurements and pH adjustments were carried out using an Elico digital pH-meter Model LI-127. All weighing operations were done by using Tapson's analytical single pan balance model 200 T having 0.001 g accuracy.

2.2. Reagents

2.2.1. Standard samarium(III) solution (1 mg mL^{-1})

Samarium(III) stock solution 1 mg mL^{-1} was prepared by dissolving 1.160 g of samarium oxide in 5 mL hot hydrochloric acid (1:1) and diluted to 1000 mL with distilled water. The solution was standardized (Welcher, 1958) and used by diluting it as required.

2.2.2. Triethanol amine buffer solution (pH 7.2)

Triethanolamine buffer solution was prepared by mixing 200 mL of triethanolamine (15%, w/v) with 160 mL of 1 mol dm^{-3} nitric acid and 40 mL of water. The pH of mixture was adjusted to 7.2 ($\pm$0.1) using dilute ammonia and nitric acid solutions.

2.2.3. Arsenazo I (0.05%, w/v)

Aqueous solution of Arsenazo I (0.05%, w/v) was prepared and used for the spectrophotometric determination of samarium(III).

2.2.4. 2-Octylaminopyridine (2-OAP)

The extractant 2-OAP was prepared by the method of Borshch and Petrukhin (1978) and its 0.025 mol dm^{-3} solution was prepared in xylene.

Unless otherwise stated, all reagents used were of analytical grade and their solutions were prepared using double distilled water.

2.3. Extraction and determination procedure for samarium(III)

The aqueous phase containing 50 μg samarium(III) was maintained at 0.01 mol dm^{-3} sodium salicylate and pH was adjusted to 8.0 with dil hydrochloric acid and sodium hydroxide solution by maintaining total dilution volume to 25 mL and transferred to 125 mL separatory funnel. A 10 mL of 0.025 mol dm^{-3} 2-OAP in xylene was added into the separatory funnel and equilibrated for 4 min and the two phases were allowed to separate. Samarium(III) from the organic phase was stripped with 0.5 mol dm^{-3} nitric acid (3×10 mL) solution.

The stripped solution containing samarium(III) was evaporated to moist dryness and extracted into water. To this solution 1 mL of 0.05% Arsenazo-I was added, the pH was adjusted to 7.2 ($\pm$0.1) by adding 2 mL of triethanolamine buffer solution. The absorbance was measured at 575 nm wavelength using the reagent blank solution.

All procedures of the extraction were carried out at room temperature 298 K. In these experiments percentage extraction (%E) was determined as follows:

$$\text{Percentage extraction } (\%E) = \frac{[A_1 - A]}{[A_1 - A_0]} \times 100$$

where A_0 is the absorbance of arsenazo I solution without cation, A_1 is the absorbance of the arsenazo I solution containing known concentration of the cation before the extraction and A is the absorbance of the arsenazo I solution containing known concentration of cation after extraction.

The distribution ratio (D) was calculated as,

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

where the V_w is the volume of aqueous phase (25 mL) and V_0 is the volume of organic phase (10 mL).

The percentage stripping (%S) values were determined by using relation,

$$\text{Percentage stripping } (\%S) = \frac{\text{Amount of metal stripped by strippant}}{\text{Amount of metal extracted}} \times 100$$

3. Results and discussion

3.1. Effect of pH

The relationship between pH variation and samarium(III) extraction efficiency was analysed and represented as extraction isotherm as shown in Fig. 1. The curve indicates the maximal extraction of 50 μg samarium(III) takes place in 7.5–10.0 pH range from 0.01 mol dm^{-3} sodium salicylate solutions, which implies favourable formation of the more stable ion-pair complex. Hence all extractions were carried out at pH 8.0. There is a possibility of hydrolysis at these pH values since it is a particular tendency of trivalent lanthanide elements. However, the physical phenomenon that characterized the hydrolysis were not observed in the stoichiometric study of extracted metals species (Fig. 2).

3.2. Effect of reagent concentration

2-Octylaminopyridine dissolved in xylene with varying concentrations from 0.005 to 0.5 mol dm^{-3} were employed to optimize the extraction conditions of 50 μg of samarium(III) at the pH 8.0. It was found that 10 mL of 0.020 mol dm^{-3} 2-OAP was sufficient for the quantitative extraction of 50 μg of samarium(III) from 0.01 mol dm^{-3} sodium salicylate solutions but in actual experiment we used 10 mL of 0.025 mol dm^{-3} 2-OAP in xylene to ensure the complete extraction of metal ion. The excess of reagent concentration (>0.150 mol dm^{-3}) affected the percentage extraction of metal ion (Table 1).

The slope of log–log linear relationships between concentrations of extractant with the corresponding distribution ratios of samarium were found to be around one in the

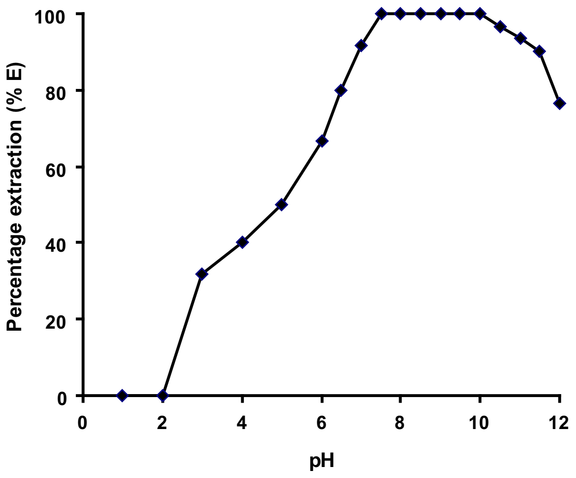

Figure 1 Effect of pH on extraction of samarium(III).

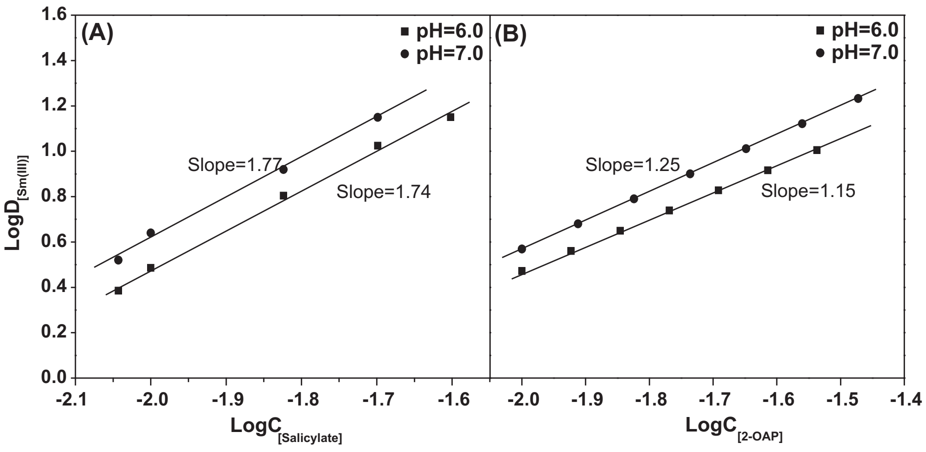

Figure 2 (A) Plot of log $D_{[\mathrm{Sm(III)}]}$ against log $C_{[\mathrm{salicylate}]}$ at 0.025 mol dm^{-3} 2-OAP. (B) Plot of log $D_{[\mathrm{Sm(III)}]}$ against log $C_{[\mathrm{2\text{-}OAP}]}$ at 0.01 mol dm^{-3} salicylate.

Table 1 Extraction of 50 μg of samarium(III) as a function of 2-OAP concentration in xylene, sodium salicylate = 001 mol dm^{-3}, aq:org = 2.5:1, pH = 8.0, equilibration time = 4 min, strippant = 0.5 mol dm^{-3} nitric acid (3 × 10 mL) at 298 K.

2-OAP concentration (mol dm^{-3})	Percentage extraction (%*E*)	Distribution ratio (*D*)
0.000	3.0	0.08
0.005	83.3	12.47
0.010	91.7	24.30
0.015	96.3	65.06
0.020	100.0	∞
0.025*	100.0	∞
0.030	100.0	∞
0.035	100.0	∞
0.040	100.0	∞
0.045	100.0	∞
0.050	100.0	∞
0.150	100.0	∞
0.250	98.3	144.55
0.350	70.0	5.83
0.500	66.7	5.01

* Recommended for general extraction procedure.

investigated system (Fig. 2(B)). This indicates the participation of one molecule of 2-OAP in the extracted metals species.

3.3. Effect of weak organic acid concentration

The extraction of samarium(III) was carried out at pH 8.0 with 0.025 mol dm^{-3} 2-OAP in xylene in the presence of varying concentrations of sodium malonate, sodium succinate, sodium salicylate and sodium oxalate as weak organic acid media in the range of 0.001 to 0.1 mol dm^{-3} (Table 2). The extraction of 50 μg samarium(III) was found to be quantitative in the range of 0.008–0.02 mol dm^{-3} for sodium salicylate and 0.005–0.007 mol dm^{-3} for sodium succinate. The extraction of samarium(III) was found to be incomplete in the malonate and oxalate media. Hence, in recommended extraction procedure we used 0.01 mol dm^{-3} sodium salicylate media due to availability of large concentration range and it has low cost.

3.4. Effect of diluents

In this study, extraction of 50 μg samarium(III) was carried out by using various organic diluents of different dielectric constants. The diluents containing 0.025 mol dm^{-3} 2-OAP were used for extraction of 50 μg samarium from 0.01 mol dm^{-3} sodium salicylate solutions. It was found that the extraction of 50 μg samarium(III) was quantitative at pH 8.00 with xylene and carbon tetrachloride while there was incomplete extraction in toluene (83.9%), kerosene (59.3%), methyl *iso*butyl ketone (67.2%), *n*-butanol (73.7%), amyl alcohol (52.0%), chloroform (87.3%), 1,2-dichloroethane (70.7%) and amyl acetate (51.2%). Throughout the experiment xylene was used as solvent due to safety reasons.

We were not observed any relationship between dielectric constant of solvent used for extraction and extraction efficiency of samarium(III).

3.5. Effect of stripping agents

Samarium(III) from organic phase was stripped with the three 10 mL portions of various stripping agents at different concentrations of mineral acids, buffer solutions and some bases. Samarium(III) was quantitatively stripped with nitric acid (0.3–1.0 mol dm^{-3}), acetic acid (0.9–1.0 mol dm^{-3}) and hydrochloric acid (0.1–0.3 mol dm^{-3}) from the organic phase. However, percentage recovery of samarium(III) from organic phase was found to be incomplete with strippants like sulphuric acid, perchloric acid, acetate buffer, ammonia, sodium hydroxide and potassium hydroxide. In recommended procedure, three 10 mL portions of 0.5 mol dm^{-3} nitric acid was used for the complete stripping of loaded organic phase (Table 3).

3.6. Variation of equilibration time

The period of equilibration was varied from 0.25 to 20 min. The extraction of samarium(III) was quantitative over a period of 1.5–7 min shaking of the solution but with prolonged shaking over 7 min there was decrease in the percentage extraction of samarium(III). This may be due to the dissociation of ion-pair complex by agitation. Thus, equilibration time for 50 μg

Table 2 Effect of weak organic acid concentration on extraction of 50 µg of samarium(III) using 0.025 mol dm^{-3} 2-OAP in xylene, sodium salicylate = 0.01 mol dm^{-3}, aq:org = 2.5:1, pH = 8.0, equilibration time = 4 min, strippant = 0.5 mol dm^{-3} nitric acid (3 × 10 mL) at 298 K.

Molarity (mol dm^{-3})	Sodium salicylate		Sodium succinate		Sodium malonate		Sodium oxalate	
	%*E*	*D*	%*E*	*D*	%*E*	*D*	%*E*	*D*
0.0000	10.0	0.28	20.0	0.63	3.3	0.08	0.0	0.00
0.0010	50.0	2.00	70.0	5.83	63.3	1.64	16.7	0.5
0.0030	58.3	9.03	93.3	37.98	77.7	8.70	23.3	0.76
0.0050	86.7	16.25	100.0	∞	86.7	16.24	32.0	1.18
0.0070	95.0	23.75	100.0	∞	95.7	55.23	38.3	1.55
0.0075	98.7	184.07	90.0	22.5	96.7	72.58	45.0	2.04
0.0080	100.0	∞	88.3	18.92	95.0	47.50	52.3	2.74
0.0085	100.0	∞	90.0	22.5	83.3	12.50	58.3	3.49
0.0090	100.0	∞	88.3	18.92	71.6	6.32	60.0	3.75
0.0095	100.0	∞	88.3	18.92	70.0	5.83	59.3	3.64
0.0100	100.0*	∞	76.7	8.22	63.3	4.31	59.7	3.69
0.0150	100.0	∞	70.0	5.83	60.3	3.80	60.0	3.75
0.0200	100.0	∞	63.3	4.32	56.7	3.26	55.7	3.13
0.0300	93.3	34.98	50.0	2.50	56.3	3.22	50.0	2.5
0.0500	63.3	4.31	30.0	1.07	53.7	2.89	47.0	2.21
0.0700	50.0	2.50	10.0	0.27	50.0	2.50	42.3	1.83
0.1000	23.3	0.76	26.7	0.90	40.0	1.66	38.7	1.58

%*E* – percentage extraction.

D – Distribution ratio.

* Recommended for general extraction procedure.

Table 3 Effect of stripping agents on extraction of 50 µg of samarium(III) by using 0.025 mol dm^{-3} 2-OAP in xylene, sodium salicylate = 0.01 mol dm^{-3}, aq:org = 2.5:1, pH = 8.0, equilibration time = 4 min, strippant = 0.5 mol dm^{-3} nitric acid (3 × 10 mL) at 298 K.

Molarity (mol dm^{-3})	%*R*							
	CH_3COOH	HNO_3	HCl	H_2SO_4[a]	$HClO_4$	NaOH	KOH	NH_3
0.1	39.7	90.0	100.0	30.0	53.3	27.7	16.7	12.0
0.2	45.0	98.5	100.0	36.7	57.3	26.0	11.3	11.3
0.3	48.3	100.0	100.0	41.7	62.0	23.0	12.3	10.7
0.4	56.7	100.0	96.7	50.0	71.7	20.7	11.3	10.0
0.5	71.7	100.0*	93.3	58.3	79.3	19.0	10.7	10.7
0.6	80.0	100.0	90.3	60.0	79.7	20.0	9.7	9.7
0.7	91.3	100.0	85.0	80.0	74.7	20.7	10.3	10.0
0.8	95.0	100.0	83.3	90.0	71.7	21.0	9.0	9.3
0.9	100.0	100.0	67.0	83.3	70.0	20.3	9.7	9.7
1.0	100.0	100.0	65.0	63.3	64.3	20.3	6.7	10.3
3.0	93.3	96.7	60.0	60.0	56.7	26.0	8.3	9.7
5.0	91.0	90.0	58.3	58.7	50.0	40.0	6.7	9.0
7.0	90.0	86.0	60.3	50.0	43.3	–	–	–
10.0	83.3	70.0	53.3	36.7	30.0	–	–	–

pH%	% Recovery
(1) Acetate buffer	
3.42	98.1
4.45	93.9
5.57	96.7
(2) Water	
	27.0

%*R* percentage recovery.

* Recommended for general extraction procedure.

[a] Concentration in normality.

samarium(III) extraction was kept about 4 min throughout the study to ensure the complete extraction.

3.7. Extraction behavior of samarium(III) as a function of metal loading capacity

Varying concentrations of samarium(III) (25–2000 µg) were extracted with 10 mL portions of 0.025 mol dm^{-3} 2-octylaminopyridine in xylene from 0.01 mol dm^{-3} sodium salicylate media. It was observed that extraction of samarium(III) was quantitative up to 800 µg and further increasing concentration, decreases the extraction efficiency of 10 mL of 0.025 mol dm^{-3} 2-OAP. This study clearly indicates that 10 mL of 0.025 mol dm^{-3} 2-OAP have 800 µg as a loading capacity.

3.8. Effect of aqueous to organic volume ratio

The effect of contacting the different volume ratios of aqueous to organic phase was studied. The results indicate that the preferred aqueous/organic (A/O) phase ratio in this study must be in between 1:1 to 4:1. Extraction decreases after beyond 4:1 ratio due to the less availability of reagent. However, in the recommended procedure, the phase ratio was maintained at 2.5:1.

3.9. Stoichiometry of extracted species

The stoichiometry of extracted species was determined by analyzing the experimental data. The conventional slope analysis method was used. The nature of extracted species of samarium(III) by 2-OAP in xylene is whether mononuclear or polynuclear was investigated. By varying initial samarium(III) concentration in the aqueous phase with distribution ratio (D), it was observed that distribution ratio was independent of samarium(III) concentration which is clear indication that the extracted species is mononuclear in the whole range of experimental study.

The plot of log $D_{[\mathrm{Sm(III)}]}$ versus log $C_{[\mathrm{Salicylate}]}$ at pH 6.0 and 7.0 with 0.025 mol dm^{-3} 2-OAP concentration was a linear graph with slopes of 1.74 and 1.77, respectively [Fig. 2(A)] which revealed that two salicylate ions react with one mole of samarium(III), while the graph of log $D_{[\mathrm{Sm(III)}]}$ versus log $C_{[\text{2-OAP}]}$ at pH 6.0 and 7.0 with 0.01 mol dm^{-3} sodium salicylate concentration was a linear graph with slopes of 1.15 and 1.25, respectively [Fig. 2(B)] indicating that one 2-OAP molecule is used in the reaction process. Therefore, the probable extraction mechanism is given as,

Extraction mechanism:

$$\text{2-OAP}_{(\mathrm{org})} + \mathrm{H}^+_{(\mathrm{aq})} \rightleftharpoons [\text{2-OAPH}^+]_{(\mathrm{org})} \tag{1}$$

$$\mathrm{SM}^{3+}_{(\mathrm{aq})} + 2\,\mathrm{sal}^{2-}_{\mathrm{aq}} \rightleftharpoons [\mathrm{Sm(sal)_2}]^-_{(\mathrm{aq})} \tag{2}$$

$$[\mathrm{Sm(sal)_2}]^-_{(\mathrm{aq})} + [\text{2-OAPH}^+]_{(\mathrm{org})} \rightleftharpoons [\text{2-OAPH}^+\mathrm{Sm\ (sal)}_2^-]_{(\mathrm{org})} \tag{3}$$

The probable extracted species [2-OAPH$^+$Sm(sal)$_2^-$] formed in organic phase was stripped out by using three portions of 10 mL of 0.5 mol dm^{-3} nitric acid solution. Reactions occurring in stripping mechanism could be given as,

Stripping mechanism:

$$[\text{2-OAPH}^+\mathrm{Sm(sal)}_2^-]_{(\mathrm{org})} + \mathrm{HNO}_{3(\mathrm{aq})} \rightleftharpoons \text{2-OAP}_{(\mathrm{org})} + \mathrm{Sm}^{3+}_{(\mathrm{aq})} + \mathrm{H}^+_{(\mathrm{aq})} + \mathrm{NO}^-_{3\,(\mathrm{aq})} + \mathrm{sal}^{2-}_{(\mathrm{aq})} \tag{4}$$

3.10. Temperature effect on extraction of samarium(III)

Under constant pH, salicylate concentration and 2-OAP concentration, samarium(III) extraction was enhanced by varying temperature in the range of 308–321 K. Results shows that with the increase in the temperature, log K_{ex} values also increases. The change in log K_{ex} values with temperature are expressed by

$$\Delta \log K_{\mathrm{ex}}/\Delta(1/T) = \Delta H/(-2.303R) \tag{5}$$

The various thermodynamic parameters like ΔG and ΔS also were calculated using following relations,

$$\Delta G = -2.303\ RT \log K \tag{6}$$

$$\Delta S = (\Delta H - \Delta G)/T \tag{7}$$

where the enthalpy change (ΔH) of the extraction process were calculated from the slope of the plots of log K_{ex} versus 1000/T, with R = 8.314 J K^{-1} mol^{-1} [Fig. 3].

$$\mathrm{Slope} = -\Delta H/2.303R$$

The mean enthalpy change accompanying the ion-pair complexation was found to be 36.24 kJ mol^{-1}. Also negative values of free energy (ΔG) reveals that the extraction reaction is favourable for samarium(III) under proposed extraction conditions (Table 4).

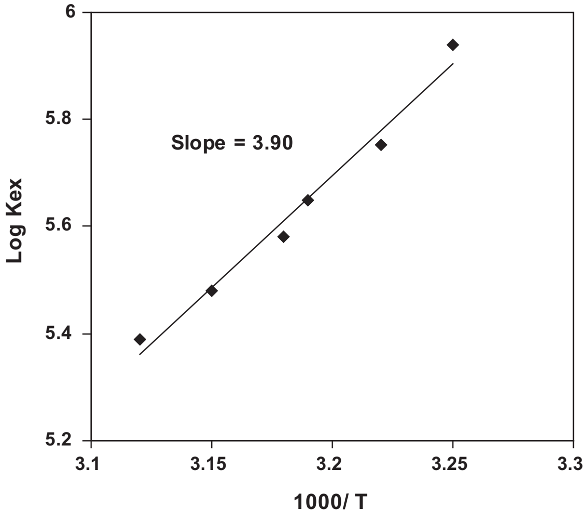

Figure 3 Effect of temperature on extraction of samarium(III).

Table 4 Effect of temperature and thermodynamic functions related to samarium(III) extraction system.

Temperature (K)	K_{ex}	Log K_{ex}	$-\Delta G$ (kJ/mol)	ΔH (kJ/mol)	ΔS (J/K/mol)
308	8.8×10^5	5.94	35.03	36.24	113.85
311	5.3×10^5	5.72	34.23		110.21
313	4.4×10^5	5.65	33.86		108.30
315	3.5×10^5	5.54	33.41		106.19
318	3.0×10^5	5.48	33.37		105.04
321	2.6×10^5	5.42	33.31		103.89

3.11. Effect of foreign ions on samarium(III) extraction system

The effect of various foreign ions was tested on the extraction of samarium(III) with 0.025 mol dm^{-3} 2-OAP in xylene as an extractant. The tolerance limit of individual foreign ions was defined as the amount of it required to cause ±2% error in the recovery of trivalent samarium using the proposed method. The results presented in the Table 5 indicate that many metal

Table 5 Effect of foreign ions on the extraction of 50 µg samarium(III) at pH = 8.0 in 0.01 mol dm^{-3} sodium salicylate with 0.025 mol dm^{-3} 2-OAP in xylene by maintaining aq:org = 2.5:1, Equilibration time = 4 min, strippant = 0.5 mol dm^{-3} nitric acid (3 × 10 mL) at 298 K.

Tolerance limit (mg)	Foreign ion added
25	Iodide, nitrite, thiosulphate
10	Acetate, thiourea, nitrate
5	Fluoride, bromate, thiocyanate
3	Malonate, sulphate, succinate, citrate, Ca(II), Mg(II)
1	Oxalate, ascorbate, Ba(II), V(V), Zn(II), Mo(VI), Tl(I), Al(III), Te(IV), Co(II), U(VI), Ce(IV)[a]
0.7	Ni(II), Cu(II), Mn(II), Mn(VII), Pb(II), Se(IV), Th(IV), Zr(IV), Nb(IV), La(III)[b], Nd(III)[c], Y(III)[a]
0.5	Cd(II), Cr(VI), Fe(III), Cr(III), Sb(III), Gd(III)[b]
0.3	Sr(II), Pd(II), Hg(II), Fe(II), Sn(II)

[a] Masked with 5 mg thiocyanate.
[b] Masked with 3 mg citrate.
[c] Masked with 5 mg fluoride.

Table 6 Binary mixture separation of samarium(III) from associated metal ions.

Metal ions	Amount taken (µg)	Average % recovery*	Chromogenic ligand	Reference
Sm(III)	50	99.7	Arsenazo -I	Marczenko (1976)
Fe(III)	500	99.5	Thiocynate	Vogel (1972)
Sm(III)	50	99.8		
V(V)	400	99.9	Hydrogen peroxide	Vogel (1972)
Sm(III)	50	99.6		
Cr(VI)	30	99.5	Diphenyl carbazide	Vogel (1972)
Sm(III)	50	99.6		
Co(II)	500	99.5	Thiocyanate	Vogel (1972)
Sm(III)	50	99.6		
Zr(IV)	200	99.4	Alizarin red S	Sandell (1965)
Sm(III)	50	99.3		
Nb(IV)	50	99.6	PAR	Marczenko (1976)
Sm(III)	50	99.0		
Ce(IV)[a]	30	99.4	Arsenazo -III	Marczenko (1976)
Sm(III)	50	99.8		
La(III)[b]	50	99.7	Arsenazo -I	Marczenko (1976)
Sm(III)	50	99.4		
Y(III)[a]	50	99.6	Arsenazo -I	Marczenko (1976)
Sm(III)	50	99.7		
Gd(III)[b]	50	99.8	Arsenazo -I	Marczenko (1976)
Sm(III)	50	99.7		
Th(IV)	30	99.4	Arsenazo -III	Marczenko (1976)
Sm(III)	50	99.5		
U(VI)	50	99.7	Arsenazo -III	Marczenko (1976)
Sm(III)	50	99.4		
Nd(III)[c]	50	99.5	PAR	Munshi and Dey (1964)

* Average of six determinations.
[a] Masked with 5 mg thiocyanate.
[b] Masked with 3 mg citrate.
[c] Masked with 5 mg fluoride.

ions do not interfere but significant interference was caused due to anions like phosphate, tartrate, and EDTA.

4. Applications

4.1. Separation of samarium(III) from associated metal ions

Based on the partition data, the separation of samarium(III) from some commonly associated metal ions like Fe(III), Cr(VI), V(V), Co(II), Th(IV), U(VI), Zr(IV), Nb(V), Y(III), La(III), Ce(IV), Nd(III), and Gd(III) using 2-OAP in xylene can be achieved by taking advantage of difference in extraction conditions.

Under the optimum extraction conditions of samarium(III), metal ions like Fe(III), V(V), Cr(VI), Co(II), Zr(IV), Nb(V), Th(IV), and U(VI), remain quantitatively unextracted in the aqueous phase and these were determined by using known methods (Marczenko, 1976; Vogel, 1972; Sandell, 1965). Samarium(III) extracted in organic phase was stripped out using 0.5 mol dm^{-3} HNO_3 and determined by using Arsenazo I method.

Since, some associated elements added, were found to be coextracted along with samarium(III), attempts were made to use different masking agents for the selective separation of the coextracted ions. Elements such as Ce(IV) and Y(III) were masked with 5 mg of thiocyanate ions, under this condition samarium(III) was quantitatively extracted and determined as described in general extraction procedure.

Samarium(III) was separated from La(III) and Gd(III) by using 3 mg of citrate ions as a masking agent while Nd(III) by 5 mg fluoride ions. The recoveries of samarium(III) and that of the added ions were obtained greater than 99.6% as shown in Table 6.

Table 7 Separation of samarium(III) from synthetic mixtures.

Metal ions	Amount taken (μg)	Percentage Recovery of Sm(III)*
Sm(III)	50	99.8
Fe(III)	500	
Cr(VI)	30	
Sm(III)	50	99.6
Cr(VI)	30	
Co(II)	500	
Sm(III)	50	99.7
V(V)	400	
Fe(III)	500	
Sm(III)	50	99.8
Fe(III)	500	
Co(II)	500	
Sm(III)	50	99.7
Th(IV)	30	
U(VI)	50	
Sm(III)	50	99.6
Zr(IV)	200	
Nb(IV)	50	

* Average of six determinations.

4.2. Separation of samarium(III) from synthetic mixtures

A ternary mixtures of Sm(III) containing transition metals like Fe(III), Cr(VI) Co(II), V(V) and some associated elements like Th(IV), U(VI), Zr(IV), Nb(V) were separated from an aqueous solution at pH 8.0 with 0.025 mol dm^{-3} 2-OAP in xylene, whereby samarium(III) is extracted while other elements remain unextracted in the aqueous phase. Then extracted samarium(III) was stripped with 0.5 mol dm^{-3} nitric acid determined by arsenazo I at 575 nm wavelength (Table 7).

5. Conclusion

The investigation led to several conclusions involving extraction mechanism for 0.025 mol dm^{-3} 2-OAP/xylene/(50 μg) samarium(III)/(0.01 mol dm^{-3}) sodium salicylate/water from 7.5 to 10.0 pH range.

1. The extraction corresponds to an anion exchange mechanism in which ion-pair of stoichiometric formula $[\text{2-OAPH}^{+}\text{Sm(sal)}_2^{-}]_{(\text{org})}$ is formed in organic phase proved by slope analysis method.
2. Developed method is efficient for quantitative separation of samarium(III) in presence of large number of various interfering cations and anions.
3. Thermodynamic functions of extraction reaction are calculated and discussed. The reaction of extracting samarium(III) is found to be spontaneous.
4. The results also demonstrates that 2-OAP has good extractability for samarium(III) in salicylate media at pH 8.0 compared with some other high molecular weight amines and organophosphorus compounds.

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