

Extraction of europium(III), americium(III) and curium(III) with DEHPA and Cyanex 272

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Received 30 November 1994; revised and accepted
20 February 1995

Extraction of Eu(III) is quantitative by 0.03 M DEHPA in xylene from 0.01 M HNO₃ solution, whereas Am(III) and Cm(III) are poorly extracted under the same condition leading to high separation factors. Cyanex 272 does not extract Eu(III), Am(III) and Cm(III) significantly even from 0.01 M HNO₃.

Several workers have reported the extraction of trivalent lanthanides and actinides with di-(2-ethylhexyl)phosphoric acid (DEHPA)¹⁻⁵. Bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) has been used to extract tervalent lanthanides⁶. In this work an attempt has been made to compare the extracting and separation ability of dialkyl phosphoric acid and dialkyl phosphinic acid in the extraction-separation of Eu(III), Am(III) and Cm(III) in nitric acid medium.

Experimental

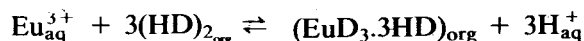
The stock solutions of ¹⁵²⁺¹⁵⁴Eu, ²⁴¹Am and ²⁴⁴Cm were used for the extraction experiments. DEHPA (Merck) and Cyanex 272 (American Cyanamid Co.) were used as received. Xylene (Merck) was used as diluent. The other chemicals were of AR grade. Prior to the extraction, pre-equilibration of the extractant in xylene and nitric acid was done. The organic phase was then equilibrated with the aqueous phase containing radio-tracer in a thermostated waterbath for 40 min. The phases were disengaged by centrifugation. Aliquots from both phases were withdrawn for radiometric assay. The purity of ¹⁵²⁺¹⁵⁴Eu and ²⁴¹Am were assayed by γ -counting using NaI(TL) scintillation detector and that of ²⁴⁴Cm was ascertained by alpha liquid scintillation counting.

Results and discussion

Extraction by DEHPA

The extraction of Eu(III) by DEHPA (0.03 M) was

carried out from 0.01-0.1 M HNO₃ solution. The extraction is found to be 97.5% at 0.01 M which gradually decreases with increase in DEHPA concentration in the range 0.005-0.3 M from 0.01 M HNO₃ solution. The plots of log D vs. log [HNO₃] (Fig. 1) having a slope of -2.7 and of log D vs. log [DEHPA] with a slope of 2.78 (Fig. 2) provide the evidence in favour of the following mechanism, since DEHPA exists as a dimer⁷.



The extraction of Am(III) by 0.03 M DEHPA from 0.01-0.1 M HNO₃ shows a gradual decrease with increase in acidity. The extraction of Am(III) was studied with varying range of concentrations of DEHPA (0.005-0.03 M) from 0.01 M HNO₃ solution. The plots (Figs 1 and 2) indicate that extraction of Am(III) by DEHPA follows the similar extraction pattern as that of Eu(III). The extraction coefficients obtained in the extraction of Cm(III) from 0.01 M HNO₃ with a varying DEHPA concentration (0.005-0.03 M) are nearly equal to those obtained in the extraction of Am(III). The plot of log D vs. log [DEHPA] (Fig. 2) with a slope of 3.1 shows the involvement of three dimers of DEHPA in the extraction of Cm(III).

Extraction by Cyanex 272

Extraction of Eu(III) by Cyanex 272 (0.15-0.4 M) from 0.01 M HNO₃ shows a regular increase with increase in Cyanex 272 concentration. It is 64.4% at 0.01 M HNO₃ with 0.4 M Cyanex 272. The plot of log

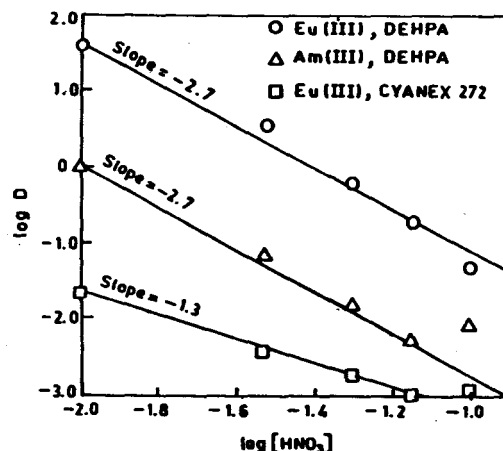


Fig. 1—Plot of log D vs. log [HNO₃] for the extraction of Eu(III) by 0.03 M DEHPA and 0.034 M Cyanex 272 and of Am(III) by 0.03 M DEHPA

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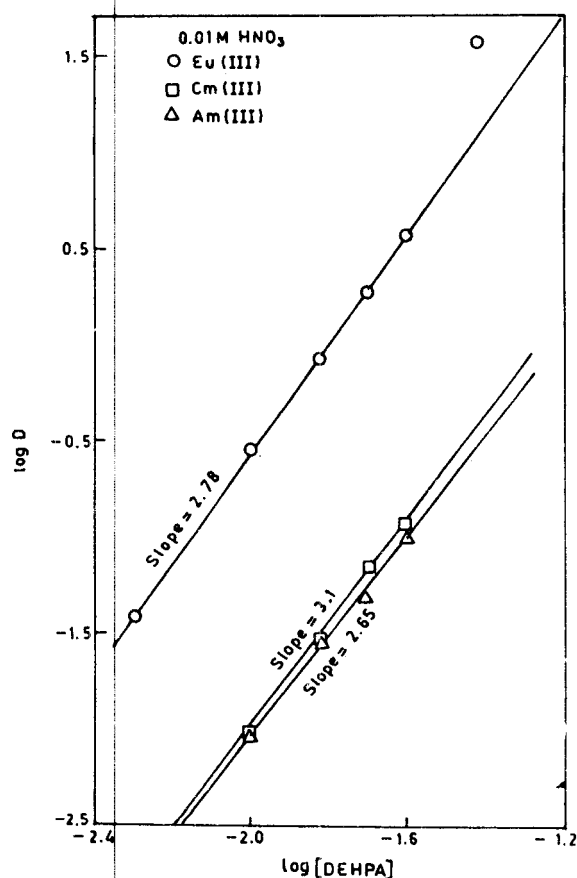


Fig. 2—Plot of log D vs. log [DEHPA] for the extraction of Eu(III), Am(III) and Cm(III) from 0.01 M HNO₃ solution

D vs. log [Cyanex 272] (Fig. 3) yields a slope of 1.76. The extraction of Eu(III) by 0.034 M Cyanex 272 in the varying acid concentration of 0.01-0.1 M HNO₃ gradually decreases with increase in acid concentration. The plot of log D vs. log [HNO₃] in the extraction yields a slope of -1.3 (Fig. 1). Extractions of Am(III) and Cm(III) from 0.01 M HNO₃ by different concentrations of Cyanex 272 (0.15-0.4 M) increase with extractant concentration but the distribution coefficients are less than that of Eu(III). The plots of log D vs. log [Cyanex 272] (Fig. 3) for the extractions of Am(III) and Cm(III) give slopes of 1.36 and 1.41, respectively.

The deviations in the values of slopes for the extractions of Eu(III), Am(III) and Cm(III) with Cyanex 272 are probably due to the neutral phosphine oxide impurities present in the Cyanex 272 sample⁸. The extractions of the above metal ions with DEHPA are found to be better than that with Cyanex 272 due to the presence of more alkyl branching in Cyanex 272 which inhibits extraction⁹.

Separation studies

The separation factors (β 's) obtained are hypothetical values deduced from the ratios of

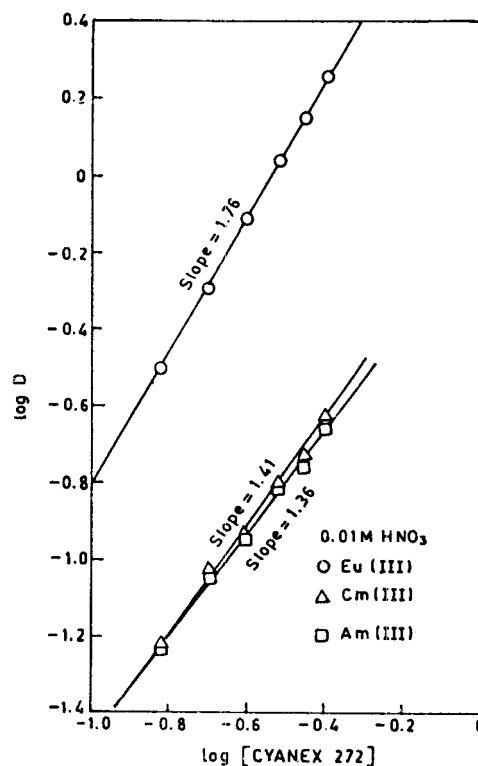


Fig. 3—Plot of log D vs. log [Cyanex 272] for the extraction of Eu(III), Cm(III) and Am(III) by Cyanex 272 from 0.01 M HNO₃ solution

distribution coefficients of the metal ions where extraction experiments were carried out under similar experimental conditions assuming that there was no mutual influence between the two species. The separation factors obtained from the above experiments are given below:

Extractants	[Extractant], M	β_1 (Eu/Am)	β_2 (Eu/Cm)
DEHPA	0.03	30.6	29.8
Cyanex 272	0.4	8.4	7.7

Acknowledgement

One of us (SM) is thankful to the CSIR, New Delhi, for the award of a junior research fellowship. We also thank Dr R H Iyer and Dr J N Mathur of Radiochemistry Division, BARC, Bombay for laboratory facilities and helpful discussions.

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