Synergistic extraction of Ce(III), Tb(III) and Lu(III) with a mixture of hexafluoroacetylacetone and triphenylphosphineoxide in benzene

By M. A. Rizvi[1], A. Ali[1,*] and M. S. Iqbal[2]

[1] Nuclear Chemistry Division, Pakistan Institute of Nuclear Science and Technology, P.O. Nilore, Islamabad, Pakistan
[2] Faculty of Science and Technology, University of Sargodha, Sargodha, Pakistan

Extraction / Ce(III) / Tb(III) / Lu(III) /
Hexafluoroacetylacetone / Triphenylphosphineoxide

Summary. The synergistic solvent extraction of trivalent lanthanides such as Ce(III), Tb(III) and Lu(III) has been studied with a mixture of hexafluoroacetylacetone (HHFA) acting as an acidic chelating agent and triphenylphosphine oxide (TPPO) as a neutral ligand in benzene from aqueous solution of pH 2.5 having ionic strength $0.01\,\text{mol dm}^{-3}$ (K^+/H^+, Cl^-). The composition of the synergistic adduct has been determined by slope analysis method and found to be $M(HFA)_3 \cdot 2TPPO$ [M = Ce(III), Tb(III) Lu(III)]. The effect of various anions and cations on the extraction of these metal ions has also been studied and only oxalate among the anion and Cr(III) among the cations has some deleterious effect. The formation constant and separation factor from various metal ions have also been determined and discussed.

1. Introduction

The synergistic effect which involves an enhancement of the extractability of a metal ion with an acidic chelating agent (HA) by the addition of a neutral ligand (S) is a well known phenomenon in solvent extraction [1]. The high extraction efficiency of lanthanides metal ions in the presence of a chelating agent and neutral donor are of great interest. Many studies regarding the synergistic extraction of lanthanides(III) with a variety of acidic chelating reagents and neutral ligands have been reported in a review by Mathur [2]. β-diketones, a class of compounds which act as an acidic chelating agent, have been mostly used for the synergistic extraction of lanthanides [3–7]. Among the fluoro-β-diketones, 2-thenoyltrifluoroacetone (HTTA) ($pK_a = 6.33$) [8] has been extensively studied for the extraction of the lanthanides and actinides using various neutral donors [2, 9–12]. However, hexafluoroacetylacetone (HHFA), having the potential of extracting the rare earth elements in low pH range due to its low pK_a value ($pK_a = 4.46$), has been paid little attention for this purpose. It has been used for the synergistic extraction of transition metals using tri-n-butylphosphate (TBP) [13, 14],

trioctylphosphineoxide (TOPO) [15] and triphenylphosphine oxide (TPPO) [16] as neutral donors. However, the work regarding the synergistic extraction of rare earth elements using HHFA and neutral donor is scanty. Only 1-10-phenanthroline [17], TOPO [18, 19] and TBP [20, 21] have been used as neutral donors. With 1,10 phenanthroline, the reported shaking time for equilibration is 1–3 h. Synergic extraction studies of rare earth elements using TOPO and TBP neutral donors with HHFA have been carried out for the analysis purpose with GC. Tetrabutylammonium ion as ion pair with HHFA in chloroform for the extraction of Eu^{+3} only from 0.1 M sodium nitrate solution has been reported [22].

In continuation of our previous work [12, 23–26], a detailed study for the extraction of rare earth elements with HHFA and TPPO in benzene was undertaken. This combination of synergic extraction, HHFA+TPPO/benzene, has not been cited in the literature for the extraction of rare earths.

This paper presents the results of the extraction of Ce(III), Tb(III) and Lu(III) as representative of the rare earth metal ions with (HHFA+TPPO)/benzene synergistic system.

2. Experimental

2.1 Material and apparatus

HHFA (Alfa, USA), TPPO and benzene from Merck (F.R. Germany) were used as such. All other chemicals used in this study were of Analar grade. The pH solutions of 1 to 3 were made by mixing appropriate quantities of $0.1\,\text{mol dm}^{-3}$ of potassium chloride and hydrochloric acid. A pH meter model 605 from METROHM Ltd., Switzerland was used for the adjustment of pH of aqueous solutions.

Radiotracers, ^{141}Ce, ^{160}Tb, ^{177}Lu, ^{60}Co, ^{203}Hg, ^{56}Mn, ^{59}Fe, ^{64}Cu, were prepared by irradiating their specpure metal or metal oxide (Johnson Matthey Chemicals Ltd. UK) separately in the research reactor PARR-1 at PINSTECH. For the preparation of ^{137}Cs radiotracer, specpure cesium carbonate was irradiated. The irradiated materials were dissolved in concentrated nitric acid separately and heated to near dryness and diluted to the required volume with deionized water. The radiochemical purity of these radiotracers was checked by a $25\,\text{cm}^3$ (Ge)Li detector coupled with a 4 K series 85 Canberra multichannal analyzer.

*Author for correspondence (E-mail: akbar@pinstech.org.pk).

2.2 Extraction procedure

Aqueous solution (2 mL) of known pH was taken in the glass culture vials with screw caps and added 50 μL of radiotracers $^{141}Ce^{3+}$, $^{160}Tb^{3+}$ or $^{177}Lu^{3+}$, having $\sim 65\,000$ to $70\,000$ counts per minute (cpm) activity separately, and then added 2 ml of organic phase, having appropriate concentration of HHFA or/and TPPO ($0.01\,mol\,dm^{-3}$) dissolved in benzene. The contents of the tube were mixed with the help of a wrist action electrical shaker (George and Griffen, UK) for five minutes. The phases were separated by centrifugation for two minutes and one mL of each phase was pippeted out and assayed radiometrically for one minute time using well type NaI (Tl) scintillation detector coupled with a counting assembly from Tennelec Inc., USA. The distribution coefficient (K_d) was determined as the ratio of the activity of the organic phase to that of the aqueous phase after subtracting the background count rate. The average background activity for ten readings was $1800 \pm 42\,cpm$. The experimental work was carried out in duplicate and the average results are presented in this paper. The overall experimental error lies within 1–5%.

3. Results and discussion

The extraction of Ce(III), Tb(III) and Lu(III) ($\sim 3 \times 10^{-5}\,mol\,dm^{-3}$) with $0.01\,mol\,dm^{-3}$ HHFA or/and TPPO in benzene, was separately studied from pH solutions (1–3) and the results are shown in Fig. 1. The extraction of these metal ions with HHFA and TPPO alone is $< 1\%$ upto pH 2.5, whereas with the mixture of HHFA and TPPO it starts increasing and becomes $\geq 99\%$ at pH 2.5. The extraction of these metal ions with the mixture of HHFA and TPPO after pH 2.5 to 3 remain constant ($> 99\%$). As the maximum synergism ($K_{d\,syn} = K_{d\,HHFA+TPPO}/(K_{d\,HHFA} + K_{d\,TPPO})$) appeared at pH 2.5, $i.e.$ 10^3–10^4, therefore, this pH was selected as the optimum pH for further experimental work. $K_{d\,HHFA}$, $K_{d\,TPPO}$ and $K_{d\,HHFA+TPPO}$ represent the distribution coefficients using organic phase containing HHFA, TPPO alone, and mixture of HHFA and TPPO, respectively.

The effect of equilibration time on the synergistic extraction of Ce (III) with $0.01\,mol\,dm^{-3}$ mixture of HHFA and TPPO in benzene from pH 2.5 solution was studied from one minute to fifteen minutes. The equilibration was achieved within 3 minutes, however, five minutes were used for the equilibration of aqueous and organic phases.

The composition of the synergic adduct extracted into the organic phase was studied by slope analysis. The plot of log D $vs.$ pH for constant concentration of Ce(III), Tb(III) and Lu(III) ($5 \times 10^{-5}\,mol\,dm^{-3}$) is shown in Fig. 2. The slopes of the plots for Ce(III), Tb(III) and Lu(III) were found to be 3.08, 3.06 and 2.96, respectively. This indicates that three conjugate base of HFA^{-1} is present per adduct to neutralize the charge of these metal ions. The plots of log D $vs.$ log[HHFA] at a constant concentration of TPPO ($0.01\,mol\,dm^{-3}$) are shown in Fig. 3. The slope of these plots appeared to be 3.02(Ce), 3.12(Tb) and 3.11(Lu), depicting that three conjugate base (HFA^{-1}) of HHFA is attached per adduct of each metal ion and no HHFA molecule is participating in the adduct formation by acting as neutral donor. Fig. 4 shows the plots of log D $vs.$ log[TPPO] at a con-
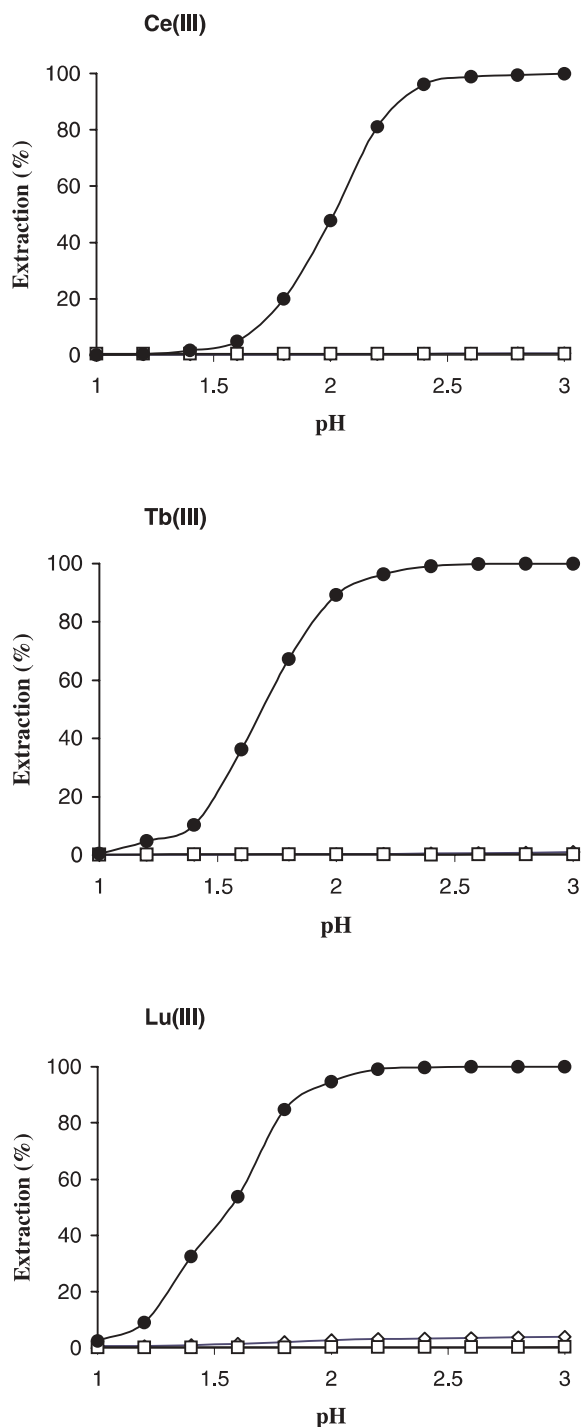

Fig. 1. Effect of pH on the extraction of Ce(III), Tb(III) and Lu(III) ($\sim 3 \times 10^{-5}\,mol\,dm^{-3}$) with $0.01\,mol\,dm^{-3}$ of HFFA (–△–), TPPO (–□–) and HFAA+TPPO (–●–) in benzene.

stant concentration of HHFA ($0.01\,mol\,dm^{-3}$) at pH 2.5. The slope of these plots appeared to be 2.08(Ce), 2.04(Tb) and 2.01(Lu), suggesting that two molecules of TPPO are present per synergic adduct acting as neutral donor. The possible composition of the synergistic adduct can be suggested as $M(HFA)_3 \cdot 2TPPO$, where M represents Ce(III), Tb(III) and Lu(III). This composition of the synergistic adduct is in good agreement with the results previously reported by Butts and Banks [27] for HHFA and TBP in cyclohexane synergic system. In our determination of the extracted complexes, the mechanism can be deduced as follows:
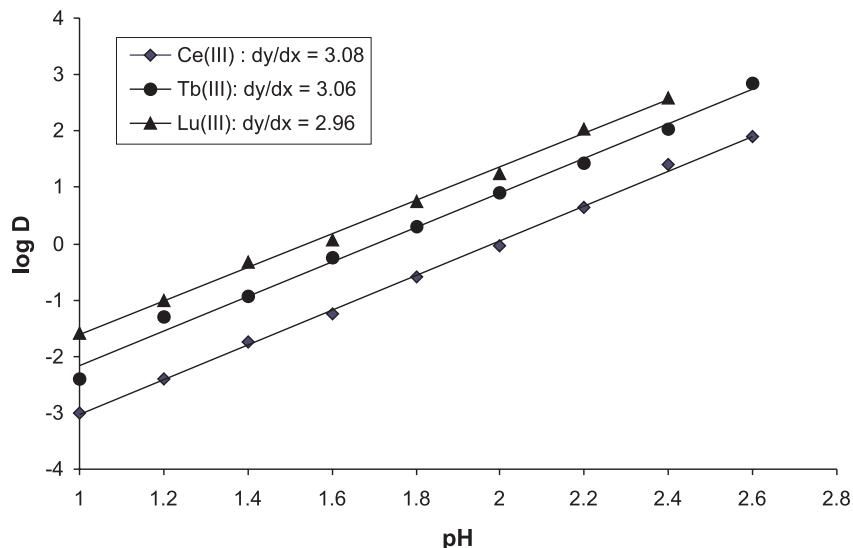
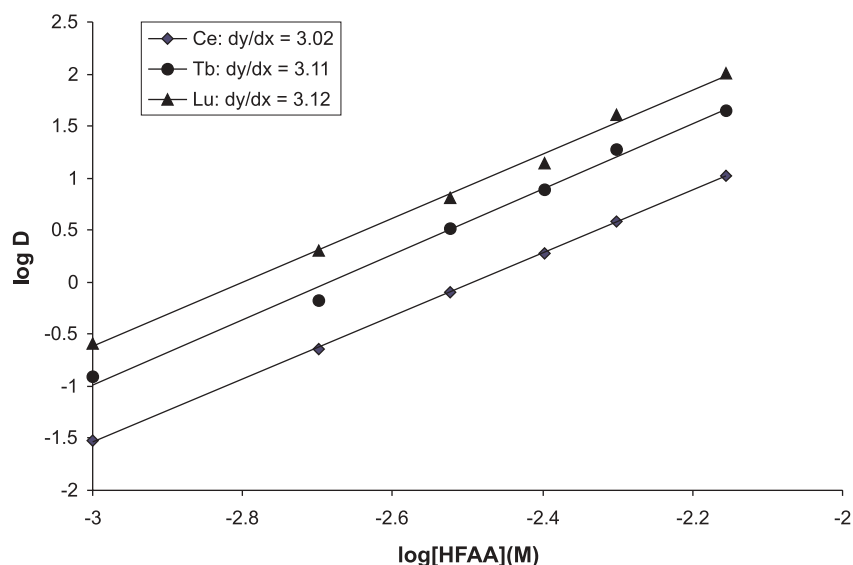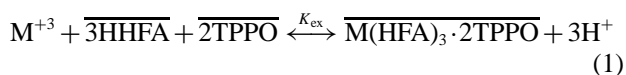**Fig. 2.** $\log D$ *vs.* pH using $0.01\ \mathrm{mol\,dm^{-3}}$ (HHFA +TPPO)/benzene as organic phase.

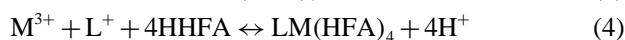**Fig. 3.** $\log D$ *vs.* $\log[\mathrm{HHFA}]$ at constant concentration of TPPO ($0.01\ \mathrm{mol\,dm^{-3}}$) in benzene.

$$\mathrm{M^{+3}} + \overline{\mathrm{3HHFA}} + \overline{\mathrm{2TPPO}} \xrightarrow{K_{ex}} \overline{\mathrm{M(HFA)_3 \cdot 2TPPO}} + \mathrm{3H^+} \tag{1}$$

$$K_{ex} = K_d[\mathrm{H^+}]^3/[\mathrm{HHFA}]^3[\mathrm{TPPO}]^2. \tag{2}$$

Where M and the expression under bar (———) represent the rare earth metal ion and the species in the organic phase, respectively. The equilibrium constant ($\log K_{ex}$) was calculated to be 3.68 ± 0.06, 4.69 ± 0.04 and 5.3 ± 0.3 for Ce(III), Tb(III) and Lu(III), respectively, using Eq. (2). The equilibrium constants deduced refer only to the concentration quotients calculated on the basis of the activity coefficients of the species involved; they do not change significantly under the experimental conditions.

Previously it was reported that a molecule of HTTA or acetylacetone (β-diketone) could function as a neutral donor during solvent extraction [28]. Complexes of composition, $\mathrm{LM(HFA)_4}$, where L is an alkali metal and M is a rare earth metal, have also been prepared [29]. The formation of a ternary complex of $\mathrm{EuA_4^-}$ (tba$^+$), where A is a β-diketone and tba is a tetrabutylammonium ion, was reported by Noro and Sekine [22]. The pH and HHFA concentration dependence results obtained in the present study indicate that the

following reactions do not occur during the extraction of the rare earths in the presence of TPPO.

$$\mathrm{M^{3+}} + \mathrm{4HHFA} \leftrightarrow \mathrm{M(HFA)_3 \cdot HHFA} + \mathrm{3H^+} \tag{3}$$

$$\mathrm{M^{3+}} + \mathrm{L^+} + \mathrm{4HHFA} \leftrightarrow \mathrm{LM(HFA)_4} + \mathrm{4H^+} \tag{4}$$
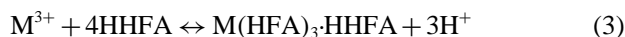
The possible reason could be the low pH (2.5) of aqueous phase at which the concentration of conjugate base (HFA$^-$) is not high enough to form such type of complexes. The observed formation of tris-chelate indicated that chloride ions were not involved, as indicated by Eq. (4), in the formation of the extracted complexes.

The poor extraction of lanthanides ions with HHFA can be attributed to the formation of hydrated chelates, $\mathrm{M(HFA)_3 \cdot nH_2O}$, which limited the solubility of the complexes in the organic solvent as was the case with trifluoroacetylacetone (HTFA) [20] and acetylacetone [30]. The enhancement in the synergism may be due to the replacement of hydrated water molecules with the TPPO molecule in the tris-chelate as suggested by Mitchell [21] and the extraction mechanism can be given as:
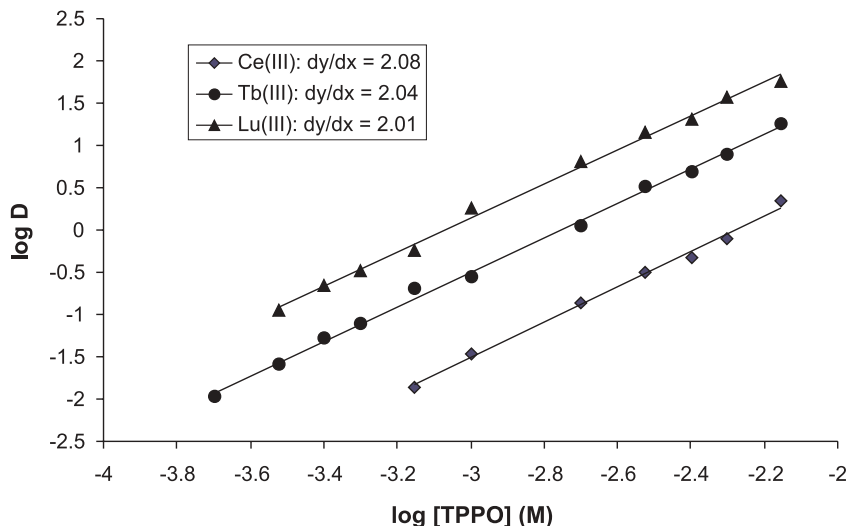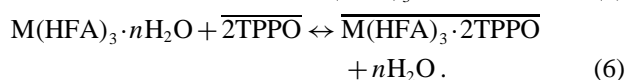
Fig. 4. log D *vs.* log[TPPO] at constant concentration of HHFA ($0.01\ \mathrm{mol\,dm^{-3}}$) in benzene.

Table 1. Effect of various anions on the extraction of Ce(III), Tb(III) and Lu(III) with $0.01\ \mathrm{mol\,dm^{-3}}$ of (HFAA+TPPO)/benzene from pH 2.5 aqueous solution.

Anion[a] (added as sodium salt)	Extraction (%)		
	Ce(III)	Tb(III)	Lu(III)
Fluoride	99.7	99.9	99.1
Citrate	99.6	99.2	99.2
Oxalate	99.7	84.3	87.5
Bromide	98.6	98.2	98.8
Hydrogenphosphate	99.8	99.4	98.8
Cyanide[b]	99.7	99.8	99.3
Thiosulphate	99.4	99.2	98.9
Acetate	99.3	99.2	99.2
Thiocyanate	99.4	99.6	99.3
Ascorbic acid	99.8	99.3	98.4
Carbonate	99.6	99.6	99.3
Tartrate	99.8	99.5	99.4

a: salt concentration $= 10\ \mu g/mL$;
b: potassium salt.

Table 2. Effect of various cations on the extraction of Ce(III), Tb(III) and Lu(III) with $0.01\ \mathrm{mol\,dm^{-3}}$ of (HFAA+TPPO)/benzene from pH 2.5 buffer solution.

Cation[a] (added as chloride or nitrate salt)	Extraction (%)		
	Ce(III)	Tb(III)	Lu(III)
Mg(II)	98.2	98.9	97.1
Zr(IV)	99.5	98.7	96.7
Co(II)	98.8	98.3	98.1
Cu(II)[b]	98.5	98.1	98.1
Mn(II)	99.8	98.7	97.6
Fe(III)	97.7	98.2	97.1
Fe(II)	98.8	97.8	97.1
Ba(II)	99.0	96.8	97.7
Cd(II)	98.8	98.5	98.6
Sr(II)	99.7	98.5	97.2
Pb(II)	98.6	98.5	97.1
Ni(II)	98.3	98.5	97.2
Cr(III)	99.9	92.1	97.1

a: salt concentration $= 10\ \mu g/mL$;
b: sulphate salt.

$$M^{+3} + \overline{3\,\mathrm{HHFA}} + n\mathrm{H_2O} \leftrightarrow \overline{M(HFA)_3 \cdot n\mathrm{H_2O}} + 3\mathrm{H}^+ \quad (5)$$

$$\overline{M(HFA)_3 \cdot n\mathrm{H_2O}} + \overline{2\,\mathrm{TPPO}} \leftrightarrow \overline{M(HFA)_3 \cdot 2\,\mathrm{TPPO}}$$
$$+ n\mathrm{H_2O}. \quad (6)$$

The effect of various anions and cations of the extraction on the lanthanide (III) ions with HHFA+TPPO/benzene ($0.01\ \mathrm{mol\,dm^{-3}}$) from pH 2.5 aqueous solution having ionic strength $0.1\ \mathrm{mol\,dm^{-3}}$ ($\mathrm{H^+/K^+, Cl^-}$) at ~ 100 fold higher concentration of the metal of interest was studied and the results are presented in Tables 1 and 2, respectively. All the anions as their sodium salt and the cations as their chloride or nitrate salts were added except stated otherwise. Among the anions, only oxalate reduced the extraction of Tb(III) and Lu(III) to 84% and 87%, respectively, whereas Cr(III) reduced the extraction of Tb(III) to 92%. All the other cations

Table 3. Extraction of various metal ions with $0.01\ \mathrm{mol\,dm^{-3}}$ of (HFAA+TPPO)/benzene from pH 2.5 aqueous solution.

Radiotracer (mol dm^{-3})		K_d M	Separation factor K_d (Ce^{3+}) $= 39 \pm 1.4$	Separation factor K_d (Tb^{3+}) $= 275 \pm 2.4$	Separation factor K_d (Lu^{3+}) $= 696 \pm 3$
^{137}Cs^{1+}	$2.3\ \times 10^{-5}$	0.008 ± 0.0006	4.87×10^3	3.44×10^4	$8.7\ \times 10^4$
^{60}Co^{2+}	$3.4\ \times 10^{-5}$	0.017 ± 0.002	2.29×10^3	1.62×10^4	4.09×10^4
^{203}Hg^{2+}	$2.5\ \times 10^{-5}$	0.097 ± 0.0025	4.02×10^2	2.83×10^3	7.17×10^3
^{64}Cu^{2+}	2.16×10^{-5}	$0.2\ \ \pm 0.08$	1.95×10^2	1.37×10^3	3.48×10^3
^{56}Mn^{2+}	4.55×10^{-6}	$0.06\ \pm 0.005$	$6.5\ \times 10^2$	4.58×10^3	1.16×10^4
^{59}Fe^{3+}	7.85×10^{-4}	0.187 ± 0.004	2.08×10^2	1.47×10^3	3.72×10^3

Separation factor $= K_d$ REE$/K_d$ M, REE $=$ rare earth element.

and anions studied have negligible effect on the extraction of these rare earth metals ions.

The selectivity of this synergistic extraction system was examined by the extraction of various mono-, di-, and trivalent metal ions using their respective radioisotopes with $0.01 \, mol \, dm^{-3}$ (HHFA+TPPO)/benzene from pH 2.5 buffer solution using the same extraction procedure as given in the experimental section and the results are presented in Table 3. The data showed that all metal ions studied have low K_d values denoted as K_dM, and their separation factors, calculated as the ratio of the K_d values of the rare earth metal ion to the K_dM value of the metal of interest, lie in the range of 10^3 to 10^5, which indicate a good selectivity for these metal ions.

4. Conclusion

The synergistic extraction system comprising HHFA+ TPPO/benzene has been found to be a powerful extraction system for the extraction of trivalent lanthanide ions from aqueous solutions of pH 2.5. The extraction system has good selectivity for rare earth elements from many transition metals. Most of the anions and cations do not interfere in the extraction of rare earth elements.

References

1. Sekine, T., Hasegawa, Y.: *Solvent Extraction Chemistry: Fundamentals and Applications*. Marcel Dekker, New York (1977), p. 523–544.
2. Mathur, J. N.: Solv. Extr. Ion Exch. **1**, 349 (1983).
3. Carey, M. A., Banks, C. V.: J. Inorg. Nucl. Chem. **31**, 533 (1969).
4. Nakamura, S., Suzuki, N.: J. Radioanal. Nucl. Chem. Art. **99**, 145 (1986).
5. Dukove, I. L., Jordanov, V. M.: Solv. Extr. Ion Exch. **16**, 151 (1998).
6. Reddy, M. L. P., Verma, R. L., Tramamohan, T. R.: Radiochim. Acta **80**, 151 (1998).
7. Satake, S., Tsukahara, S., Suzuki, N.: Solv. Extr. Ion Exch. **17**, 259 (1999).
8. Sekine, T., Hasegawa, Y., Ihara, N.: J. Inorg. Nucl. Chem. **35**, 3968 (1973).
9. Nakamura, S., Imura, H., Suzuki, N.: J. Radioanal. Nucl. Chem. Art. **82**, 33 (1984).
10. Pruett, D. J., Clark, M. C., Ensor, D. D.: Sep. Sci. Technol. **25**, 1777 (1990).
11. Khopkar, P. K., Mathur, J. N.: Sep. Sci. Technol. **16**, 957 (1981).
12. Saeed, M. M., Ahmad, M., Ali, A., Cheema, M. N.: J. Radioanal. Nucl. Chem. Lett. **164**, 1 (1992).
13. Olaughlin, J. W., Obrien, T. P.: Talanta **22**, 587 (1975).
14. Tomazic, B. B., Olaughlin, J. W.: Anal. Chem. **45**, 1519 (1973).
15. Sekine, T., Iwahori, S., Mura, R.: J. Inorg. Nucl. Chem. **38**, 363 (1977).
16. Khalifa, S. M., Aly, H. F., Zakareia, N., Daoud, J. A.: Solv. Extr. Ion Exch. **3**, 473 (1985).
17. Nakamura, S., Suzuki, N.: Polyhedron **5**, 1805 (1986).
18. Mitchell, J. W., Ganges, R.: Anal. Chem. **46**, 503 (1974).
19. Murthy, K. S. R., Krupadam, R. J., Anjaneyulu, Y.: J. Chromatogr. Sci. **36**, 595. (1998).
20. Mitchell, J. W., Banks, C. V.: Talanta **19**, 1157 (1972).
21. Mitchell, J. W.: Synergic Solvent Extraction and Thermal Studies of Fluorinated Beta-Diketone-Organophosphrous Adduct Complexes of Lanthanide and Related Elements. Ph.D. Thesis, Iowa State University, Ames, Iowa (1970).
22. Noro, J., Sekine, T.: Bull. Chem. Soc. Japan. **66**, 1647 (1993).
23. Saeed, M. M., Ali, A., Ahmed, M., Cheema, M. N., Qureshi, I. H.: J. Radioanal. Nucl. Chem. Art. **129**, 69 (1989).
24. Saeed, M. M., Ali, A., Ahmed, M., Cheema, M. N., Qureshi, I. H.: J. Radioanal. Nucl. Chem. Art. **131**, 149 (1989)
25. Ali, A.: Radiochim. Acta **92**, 925 (2004).
26. Rehman, H., Ali, A., Anwar, J., Yawar, W.: J. Radioanal. Nucl. Chem. **267**, 421 (2006).
27. Butts, W. C., Banks, C. V.: Anal. Chem. **42**, 133 (1970).
28. Poskazer, A. M., Forman, B. N. Jr.: J. Inorg. Nucl. Chem. **16**, 323 (1961).
29. Belcher, R., Majeer, J., Perry, R., Stephen, W. I.: J. Inorg. Nucl. Chem. **31**, 471 (1969).
30. Brown, W. B., Steinback, J. F., Wagner, W. F.: J. Inorg. Nucl. Chem. **13**, 119 (1960).