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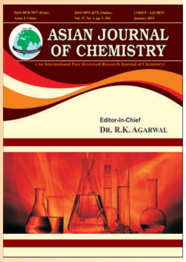

Synergic Extraction of Europium(III) with 1 M Mixture of Di-*n*-butylsulfoxide and *Bis*(2,4,4-Trimethylpentyl)phosphinic Acid in Chloroform and its Subsequent Determination by Using Arsenazo(III) as Chromogenic Reagent

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Synergistic extraction method has been developed for the extraction of Eu(III) from buffer solution of pH 3 using 1 M synergic mixture of di-*n*-butylsulfoxide (DBSO) and Cyanex-272 in chloroform. The extracted europium was measured spectrophotometrically by using 0.01 % solution of arsenazo(III) in 3 M perchloric acid as chromogenic reagent. Various parameters such as pH, shaking time, extractant metal ion concentration, cationic, anionic effects and temperature effects were optimized on extraction of Eu(III) among various cations. Only Sr(II), Ni(II) and Fe(III) interfere in the extraction process. Anions such as fluoride, oxalate and thiosulphate interfere on extraction of Eu(III). Deionized water was found to be the most suitable stripping agent for europium back extraction due to its economical suitability and easy and comparatively good refining of europium from organic phase. The extraction was found to be almost independent of the metal ion concentration in the range studied (6.6×10^{-4} to 6.58×10^{-3} M). The composition of the extracted species was found to be $Eu(C272)_3 \cdot 2DBSO$.The accuracy of the method proposed has been checked by determining concentration of standard europium solution in the range of 100-4000 ppm. It was noted that per cent deviation decrease with increasing concentration of metal ions. The recycling capacity of the organic solvent was checked and found to be excellent without any degradation.

Keywords: Synergic extraction, Europium(III), Di-*n*-butylsulfoxide.

INTRODUCTION

Due to sizeable cross-sections for slow neutron capture characteristic of europium, it is thus of interest and important in controlling the neutron fluxes in nuclear reactors[1]. Europium is even more effective as compared to cadmium, a well know substance used for neutron capture because of its low rate of burn off. Individual europium nuclide undergo (n, γ) capture reactions, yielding each time species of larger masses but of comparably larger cross-sections. Radionuclide of europium have also been proved useful particularly as tracers in the analysis of complex mixtures and in the resolution of these mixtures by ion-exchange and solvent extraction techniques[2]. Due to its importance in nuclear reactor control rods and as tracers in many analyses much work has been done for europium purification and extraction. According to the recent literature survey extraction behaviour of europium has been deeply studied. Since synergistic extraction was found in 1950, a number of studies have been reported.

Solvent extraction of Eu(III) with 4-thiobenzoyl-2,4-dihydro-5-methyl-2-phenyl 3*H*-pyrazol-3-one (SBMPP) and thiobenzoyl trifluoroacetone (SBTA) was studied by Chouhan and Rao[3]. Eu(III) was extracted from buffered aqueous media into benzene as $Eu(SBMPP)_3$ and $U(SBTA)_3$ chelates. The effect of phosphorus esters, trioctyl phosphine oxide (TOPO) and tributyl phosphate (TBP) and heterocyclic bases, pyridine, γ-picoline and quinoline as auxiliary ligands on the extraction of Eu(III) was studied. A large synergistic enhancement was observed in all systems[3]. Jyothi and Rao[4] has investigated the extraction behaviour of La(III), Ce(III), Eu(III), Th(IV) and U(VI) with 3-phenyl-4-benzoyl-s-isoxazolone (HPBI) in chloroform. The mechanism of extraction and the species extracted was identified. Extraction constants for each system were calculated. A comparison of the extraction constants with those for the 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) and thenoyl trifluoro acetone (HTTA) systems indicate that 3-phenyl-4-benezoyl-s-isoxazolone (HPBI) extracts these metal species better than HPMBP and HTTA do[4]. Solvent extraction of Eu(III) from nitrate medium (0.1 M or 1 M) with acidic chelating extractants HL in chloroform, at 25 °C has been studied by Arichi *et al.*[5]. The extractants are either 3-phenyl-4-acylisoxazol-5-one or substituted 4-acyl-5-hydroxypyrazoles. 1-(*p*-Nitro-phenyl)-3-

phenyl-4-lauryl-5 hydroxypyrazole (HNPPLP) and 1-phenyl-3-methyl-4-(*p-tert*-butylbenzoyl)-5-hydroxy-pyrazole (HPMtbBP) of various acidities. In all cases europium is extracted by cation exchange as EuL_3. Because of their higher acidities extractions performed with 4-acylisoazol-5-ones occur at lower pH range than with 4-acylpyrazol-5-ones.The nature of the cation of inorganic salts used to fix the ionic strength has no effect on the extraction[5]. The extraction of Am^{3+} and Eu^{3+} from picric acid solution by N,N-1,2-ethanediyl-*bis*[2-(N,N-diphenyl-carbamoyl-methoxy)benzamide] was investigated by Fan *et al.*[6] by using a radioactive tracer technique. The effect of various parameters such as pH, organic diluents, different extractants, picric acid and extractant concentration on the extraction of Am^{3+} and Eu^{3+} has been studied[6]. Noro and Sekine[7] reported the solvent extraction of Eu(III) with benzoylacetone and benzoyl trifluoroacetone into CCl_4 in the presence and absence of tetrabutylammonium ions. The solvent extraction of europium(III) in 0.1 M sodium nitrate solutions with benzoylacetone (Hbza) or benzoyl-trifluoroacetone (Hbfa) in CCl_4 was measured in the presence and absence of tetrabutylammonium ions. Although extraction with benzoyl-trifluoroacetone (Hbfa) occurred at lower pH than with benzoyl-acetone (Hbza) the extraction measured as a function of β-diketonate ion concentration in the aqueous phase was rather similar[7]. The liquid-liquid extraction of some trivalent rare earths Ln(III) (Ln = La, Eu, Lu), performed from 0.1 M $NaNO_3$ aqueous solution by (HL-10-LH) and (HL-4-LH) in chloroform has been studied by Maroun *et al.*[8]. The process of extraction has been determined by the slope analysis method. Zamani and Yaftian[9] have shown that the separation of thorium, lanthanum and europium ions has been improved by acidic extractant *bis*(2-ethylhexyl)phosphoric acid (DEHPA) in cyclohexane using 2-nitrobenzo-18-crown-6 (NB18C6) as a selective masking agent. NB18C6 was efficient masking agent towards lanthanoid ions and a better separation was obtained as compared to 18C6[9]. Solvent extraction of tetravalent thorium and trivalent europium ions from nitrate media into dichloromethane solution of triphenyl phosphine oxide (TPPO) has been studied by Yaftian *et al.*[10]. The extractant was shown to be more efficient for europium than for thorium. While the extraction of europium is controlled by enthalpy changes, the extraction of thorium is an endothermic process and is driven by entropy changes[10]. The separation of europium from a middle rare earth concentrate by combined chemical reduction, precipitation and solvent extraction methods was investigated by Preston and Preez[11] using reagents comprising reactive metals, metal amalgams, metal hydride and nitrogenous reductants. Solvent extraction of the trivalent rare earth impurities into solution of commercial organic phosphorus or carboxylic acids in xylene increased the europium content to 99.98 %[11]. Synergistic extraction of europium(III) with PTA and 1,10-phenanthroline has been examined in several organic solvents by Matsubayashi and Hasegawa[12]. It has been pointed out that when the concentration of water dissolved in hexane, benzene and carbon tetrachloride is introduced into the constants, the constants are almost independent of the solvents[12]. Awwad *et al.*[13] have reported the extraction of Eu(III) from nitrate medium by Cyanex-921. The relation between the shaking time and per cent extraction was studied at different pH. It was noted that maximum extraction of Eu(III) was found after 5 min at pH 3. Solvent extraction of thorium(IV), uranium(VI) and europium(III) by three aromatic extractants 3,5-didodecyl pyridinium nitrate (35 PY), 2,6-didodecyl pyridinium nitrate (26 PY) and 1-methyl-3,5-didodecyl pyridinium iodide (1 M 35PY) has been studied in nitric acid media by Ensor[14]. The overall extraction efficiency of the metal ions[14] was $Th^{4+} > UO_2^{2+} > Eu^{3+}$. Hala and Babakova[15] have investigated extraction of Eu(III) with HMPTA. The species extracted was found to be $Eu(NO_3)_3 \cdot 3HMPTA$. In presence of TBP a weak synergism is observed due to the formation of mixed solvates $Eu(NO_3)_3.(HMPTA)_{3-1}.(TBP)_1$[15]. Bhatti[16] has studied the temperature effect on synergistic extraction of Eu(III) by HTTA in the presence of 2,2-bipyridyl and 1,10-phenanthroline from sodium acetate buffer solution 4.2. Extractions were carried out at 15,25 and 35 °C. It was observed that the increasing temperature favored the extraction of Eu(III) by HTTA alone while the reverse was true for synergic extractions[16]. Synergistic extraction of trivalent Eu, Gd and Am from aqueous perchlorate medium has been studied by Shehata *et al.*[17] using mixtures of HTTA and Ce in chloroform at 25 °C. Slope analysis of the extraction results indicated a general formula of $M(TTA)_3,(Ce)_2$ for the extracted species. The synergic factors, extraction constants and formation constants of the extracted species were determined and discussed[17]. Physical properties of the organic phase in an extraction system relates to the species formed, while the composition of this phase varies. Important information is obtained from the variation of composition itself and from the maximal amounts of solutes that may be extracted into a given quantity of solvent. Much of this methods has been made in studies of extraction of metal complexes where definite complex species are formed *e.g.* the $U^{IV}–Cl^-–TBP$ system[18] or $U^{VI}–NO_3–TOA$ system[19]. Care must however, be taken with this method in particulars with aggregated extractants, since in some cases large loading numbers that is extractant-to-distributed ratios, result in the saturated solution, without indicating the true composition of a complex species. In the extraction of uranium(VI) from sulfuric acid with trioctyl-ammonium (TOA) sulphate solution[20], uranium can be loaded into the organic phase up to a ratio TOA: U of 5, while plutonium(VI) can be extracted with this reagent from nitric acid[19], up to ratio TOA: Pu of 4, in both cases there is good evidence that the species formed are not $(R_3NH)_5UO_2(HSO_4)_7$ and $(R_3NH)_4Pu(NO_3)_3$ as deduced form these ratios. Much use has also been made of spectral measurement on organic extracts to give information on the species extracted. In every case where the distribution of species at macro concentrations can be studied and for all new and no sufficiently well-known extractants, physical measurements on organic phase can yield much important information and should always be carried out. Synergism is essentially an organic-phase reaction in which the extractive power of the extractants changes when in the presence of one another and also the composition of the metal-bearing species in the organic phase is not the same as in the case of a one extractant system. There are four different types of synergistic combinations. Two of them involve one acidic and one neutral extractant, while the third and fourth groups involve the combination of two neutral and two chelating extracting agents respectively.

Cunningham and coworkers[21] have demonstrated that tri- and tetravalent actinides and europium form various mixed complexes under certain conditions for example, while TBP with Am(TTA)$_3$ or Eu(TTA)$_3$ forms synergistic adducts of the M(TTA)$_3$S$_2$ type under similar experimental conditions TBPO will form the synergistic adduct M(TTA)$_2$NO$_3$S$_2$ when extracted from nitric acid media[22]. Distribution data indicated that the formation of M(TTA)$_3$S$_2$ does not take place to any considerable extent. Irving and Edgimgton[23,24] argued that the coordination number of trivalent lanthanides and actininides may rise to eight in order to accommodate the neutral ligand molecules. Considering all these examples the possible composition of the synergistic adduct formed when Eu(III) is extracted by using 1 M synergic mixture of Di-*n*-butyl sulfoxide (DBSO) and Cyanex-272 (acidic) in chloroform at pH-3 may be Eu(C272)$_3$·2DBSO.

EXPERIMENTAL

Double wavelength/double beam digital spectrophotometer model-1601, Shimadzu of Japan, was used for the measurement of the absorbance. For heating purpose electrical balance Sertorious of Germany was employed. pH meter (M1 151 pH/ Orp/temp) and flask shaker model SF-1, Stuart of UK are also used. Technical grade DBSO (96 %)/Cyanex-272 and reagent grade chloroform were procured from Aldrich chemical Co., USA. Arsenazo(III) (0.01 %) solution in 3 M HClO$_4$ was prepared by dissolving a weighed quantity of arsenazo(III) from E-Merck, Germany as such without further purification. Perchloric acid (70-72 %) of reagent grade from E-Merck Germany was used. A stock solution of europium was prepared by dissolving a weighed amount of 99 % pure europium oxide in 1 M HNO$_3$. Buffer solution of pH 3 was prepared by mixing appropriate amount of 1 M sodium acetate and 10 M hydrochloric acid using pH meter.

Extraction procedure: Extraction of Eu(III) was carried out at 25 ± 1 °C. A known amount of Eu(III) was taken in a 50 mL pyrex glass beaker and heated to near dryness on an electric hot plate. On cooling, 3 mL of the buffer solution of pH 3 was added into it and mixed well. One mL of this solution was drawn out as reference before extraction in a 50 mL Pyrex glass beaker. The remaining 2 mL aqueous solution was equilibrated with an equal volume of synergic mixture of both 1 M DBSO and Cyanex-272 in chloroform for 7 min and then centrifuged for 3 min for phase separation. Then, 1 mL of the aqueous solution was taken in another beaker (after extraction). Both solutions (before and after extraction) were heated to near dryness with 2-3 mL of concentrated perchloric acid. On cooling the beakers 5 mL of arsenazo(III) (0.01 %) solution was added and mixed well for colour development. The reagent blank was prepared under identical conditions except that it did not contain metal ions. The concentration of Eu in aqueous phase was spectrophotometrically measured using a Shimadzu UV-visible spectrophotometer model UV-1601. Europium concentrations were determined in the aqueous phase through the colour of the complex at 651 ± 2 nm. The concentration of the investigated metal in the organic phase was calculated by the difference between the concentration in the aqueous phase before and after extraction. The distribution ratio (D) for each sample was calculated from the relation:

$$D = \frac{\text{Concentration of Eu(III) in the organic phase}}{\text{Concentration of Eu(III) in the aqueous phase}}$$

The percentage extraction was calculated by the following equation:

$$E\ (\%) = \frac{100D}{D+1}$$

All the results were taken as average of the triplicate measurements.

Optimization of parameters for extraction: Various sets of experiments were designed and performed for the study of various parameters essential for the synergic extraction of europium by using a mixture of DBSO and Cyanex-272 in chloroform from buffer solutions. These include the influence of pH, shaking time, extractant (DBSO + Cyanex-272), metal ion concentration, salting out agents, temperature and interference of commonly occurring diverse ions on the extraction of europium. The method adapted for these experiments is briefly described below.

Effect of pH on the extraction: Europium standard solution (320 ppm) was taken in a set of 50 mL pyrex glass beakers and heated to near dryness on an electric hot plate. Three mL of buffer solutions of varying pH *i.e.* 1-6 were added to it. These were then mixed thoroughly and 1 mL of each solution was taken in 50 mL pyrex glass beakers as reference before extraction. The remaining aqueous solution was equilibrated mechanically in (16 × 125 mm) pyrex glass culture tubes with equal volume of 1 M synergic mixture of DBSO and Cyanex-272 in chloroform for 7 min. These were then centrifuged for 3 min for phase separation. The absorbance of europium in both phases was determined spectrophotometrically. The graph was drawn between per cent extraction of europium and varying pH.

Effect of shaking time: The standard solution of europium (320 ppm) was taken in a set of 50 mL Pyrex glass beakers and heated to near dryness on an electric hot plate. 3 mL of buffer solution of pH 3 was then added to these beakers and mixed well. 1 mL of this aqueous solution was taken in another 50 mL Pyrex glass beaker as reference before extraction. The remaining aqueous solutions were taken separately in (16 × 125 mm) culture tubes with equal volume of a mixture of 1 M DBSO and Cyanex-272 in chloroform and shaken mechanically for 1-10 min separately. The solutions were then centrifuged for 3 min for phase separation. Distribution coefficient for europium (before and after extraction) was calculated. A curve was drawn between per cent extractions of europium *versus* shaking time and results were calculated using this curve.

Effect of extractant concentration: Synergic mixture (DBSO, Cyanex-272/chloroform) of various moralities were prepared by an appropriate dilution of DBSO and Cyanex-272 with chloroform in 25 cm^3 measuring flasks. Europium standard solution (320 mg/L) was taken in a 50 mL Pyrex glass beaker and heated to near dryness. Then 3 mL of the buffer solution of pH 3 was added in each beaker and mixed well. 1 mL of each aqueous solution was pippetted out in a separate set of glass beakers as reference before extraction. The remaining 2 mL of each of the aqueous solutions was equilibrated in pyrex glass culture tubes with equal volumes of 0.3-1.50 M synergic mixture of DBSO and Cyanex-272/chloroform for 7 min. These were centrifuged for 3 min for phase separation. For determination of distribution coefficient of europium in both aliquots (before and after extraction), spectrophotometric method was adopted. The relation between per cent extraction of europium *versus* varying molarities of synergic mixture of DBSO and Cyanex-272 in chloroform was depicted graphically.

Effect of temperature: The extraction of europium with 1 M synergic mixture of DBSO and Cyanex-272 in chloroform at various temperatures (25-50 °C) was studied. Gallenkamp Thermostirrer-100 (Model BKL-235) water bath was used for maintaining constant temperature of each solution for at least 1 h. A known amount of europium was taken in a set of 50 mL pyrex glass beakers and heated to near dryness. On cooling, 3 mL of buffer solution was added in each beaker and mixed well. 1 mL of each of these aqueous solutions was pippetted out as reference before extraction, the remaining aqueous solution from each beaker was taken separately in pyrex glass culture tubes and equilibrated mechanically with equal volumes of 1 M synergic mixture of DBSO and Cyanex-272 in chloroform for 7 min. These were then allowed to stand for phase separation. Europium contents were determined in both sets of aliquots (before and after extraction). The per cent extraction of europium was plotted against varied temperature (25-50 °C).

Influence of metal ions concentration: Europium standard solutions of varying concentrations ($6.6 \times 10^{-4} - 6.58 \times 10^{-3}$ mol/dm^3) in known amounts were taken separately in a set of 50 mL pyrex glass beakers and heated to near dryness. On cooling, 3 mL of buffer solution was added separately in each beaker and mixed thoroughly. 1 mL of each solution was then pippetted out in 50 mL pyrex glass beakers as reference solutions before extraction. The remaining aqueous solutions were equilibrated with equal volumes of extractants in a mechanical shaker for 7 min. These were then centrifuged for 3 min for phase separation. For determination of europium contents in both solutions (before and after extraction) spectrophotometric method using arsenazo(III) solution as chromogenic reagent was adopted.

Effect of common cations and anions: A known amount of europium solution was taken in a set of 50 mL pyrex glass beakers and heated to near dryness. On cooling, 3 mL of buffer solution were added to each beaker and mixed well. Nitrates and chlorides of various cations of known weight (10 mg/cm^3) were added separately in these beakers and mixed thoroughly. 1 mL of the aqueous solution containing cations from each beaker was separated as reference before extraction. The remaining aqueous solutions were then equilibrated with equal volumes of 1 M synergic mixture of DBSO and Cyanex-272 in chloroform for 7 min. These were centrifuged for 3 min for phase separation. The distribution coefficient of europium in both solutions (before and after extraction) was determined spectrophotometrically.

A known amount of europium was taken in a set of 50 mL pyrex glass beakers and heated to near dryness. 3 mL of buffer solution was added to each of this beaker. Known weights (10 mg/cm^3) of sodium and potassium salts of various anions were added to these beakers separately to study their effect on the extraction of europium with 1 M synergic mixture of DBSO and Cyanex-272 in chloroform. The procedure adopted for extraction of europium was same as described earlier for the study of the effect of cations.

Influence of salting-out agents: A known amount of europium was taken in a set of 50 mL pyrex glass beakers and heated to near dryness. Three mL of buffer solution was added to each of this beaker and mixed thoroughly with known weights (10-150 mg/3 mL) of $Al(NO_3)_3.6H_2O$ as salting-out agent. 1 mL of each of these solutions was pippetted out as reference before extraction. The remaining 2 mL of the aqueous solution from each beaker was equilibrated with equal volumes of extractants for 7 min. These were then centrifuged for 3 min for phase separation. The distribution of europium in both sets of aliquots (before and after extraction) was determined in the same way as described earlier.

Back extraction of europium: Nitric acid (0.1 M), distilled water and NH_4OH (0.1 M) were tested for the back stripping of europium subsequent to its extraction from 0.1 M synergic mixture of DBSO and Cyanex-272 in chloroform. Europium contents were back stripped from loaded organic phase, by mechanical shaking with an equal volume of stripping agents HNO_3 (0.1 M), distilled water and NH_4OH (0.1 M) separately for 3 min. The stripping process was repeated thrice. The stripped solution was reduced to known volume (5 mL) by heating on electric hot plate. Europium was determined by using the method described earlier.

Recycling of the extracting agents: The ability of DBSO and Cyanex-272 in chloroform was studied. A known amount of europium was taken in 50 mL Pyrex glass beaker and heated to near dryness. On cooling, 3 mL of buffer solution was added to it and mixed well. 1 mL of the solution was pippetted out as reference before extraction. The remaining aqueous solution was equilibrated mechanically with an equal volume of 1 M synergic mixture of DBSO and Cyanex-272 in chloroform for 7 min. 1 mL of the aqueous solution was pippetted out in another beaker. The absorbance of europium in both solutions was determined by spectrophotometric method. The loaded organic phase was separated out and europium contents were stripped from organic phase by mechanical shaking with an equal volume of deionized water for 3 min. This stripped solvent (DBSO and Cyanex-272) mixture was reused for extraction of europium from fresh buffer solution. The process of europium extraction from synergic mixture of DBSO and Cyanex-272 and its back stripping was repeated four times.

Efficiency of extraction method: The standard solution of europium of different concentrations (100-4000 ppm) were taken in a set of 50 mL pyrex glass beakers and heated to near dryness. On cooling 3 mL of buffer solution was added to it and mixed well and then equilibrated with equal volumes of extracting synergic mixture of DBSO and Cyanex-272 in chloroform in pyrex glass culture tubes for 7 min on an electric flask shaker. These were allowed to stand for 3 min for phase separation. The organic phase was pippetted out in another 50 cm^3 separating funnel for each concentration. The extraction was repeated thrice by using equal volume of fresh solvent. Arsenazo(III) solution (0.01 %) was used for spot test to ensure the completeness of extraction. Extracted europium was stripped from organic phase by equilibrating mechanically with an equal volume of deionized water for 3 min. The organic phase was collected in another 50 cm^3 separating funnel for each concentration. The stripping was repeated thrice by using equal volume of fresh deionized water and organic phase was then drained out. The aqueous solution was reduced to known volume by slow heating on electric hot plate. Europium(III) was determined spectrophotometrically by known method.

RESULTS AND DISCUSSION

Effect of pH on the extraction of europium: The per cent extraction of Eu(III) against pH in aqueous solution was determined. Fig. 1 shows the europium extraction with 1 M synergic mixture of DBSO and Cyanex-272 in chloroform is maximum at pH 3 and decreases at higher pH (beyond pH 3). This shows that per cent extraction of Eu(III) decreases with increasing pH. This may be due to decomposition of complex at higher pH. This observation indicated that reaction is efficient at low pH and extraction is quantitative.

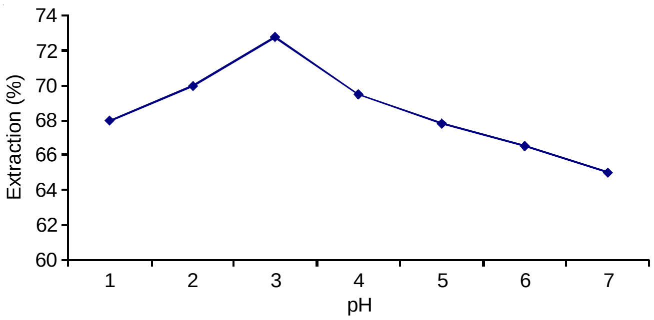

Fig. 1. Effect of pH on the extraction of europium(III) using synergic mixture of 1 M DBSO-Cyanex-272 in chloroform

Effect of equilibration period: The effect of shaking time (1-10 min) on Eu(III) extraction with 1 M DBSO and Cyanex-272 in chloroform was studied. All other parameters were kept constant. A graph was plotted between per cent extraction of europium and equilibration time. The results are shown in Fig. 2. The figure shows an increase in per cent extraction of europium with increasing shaking time up to 7 min and then decreased with increasing time. This can be explained on the basis of the facts that equilibration between europium, DBSO, Cyanex-272 in this system has attained saturation after 7 min and no further increase in extraction was observed beyond this. The study of equilibration period showed that extraction of Eu(III) using mixture of 1M DBSO and Cyanex-272 in chloroform at pH 3 is maximum within 7 min.

Effect of concentration of extractants: The effect of extractant concentration on per cent extraction of europium has been investigated by varying the concentration of synergic mixture of DBSO and Cyanex-272 in chloroform ranging from 0.1-4.4 M. All other parameters were kept constant under previously optimized conditions. Curves were constructed separately between different molarities of DBSO, Cyanex-272 and synergic mixture of DBSO and Cyanex-272 in chloroform for extraction of europium. The results are shown in Fig. 3. It was observed that per cent extraction using synergic mixture is greater than using individual extractants. The results show an increase in per cent extraction with increasing molarity of the extractant up to 1 M, then no appreciable effect was noted in the range studied. Therefore, 1 M synergic mixture of DBSO and Cyanex-272 in chloroform was used as optimum concentration for quantitative extraction of europium in the proposed extraction system.

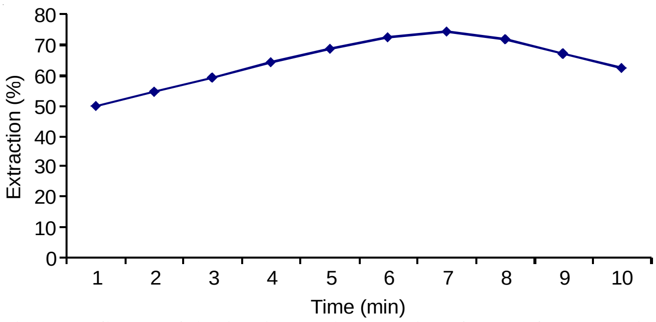

Fig. 2. Influence of shaking time on the extraction of Eu(III) from synergic mixture of 1 M DBSO-Cyanex-272 in chloroform

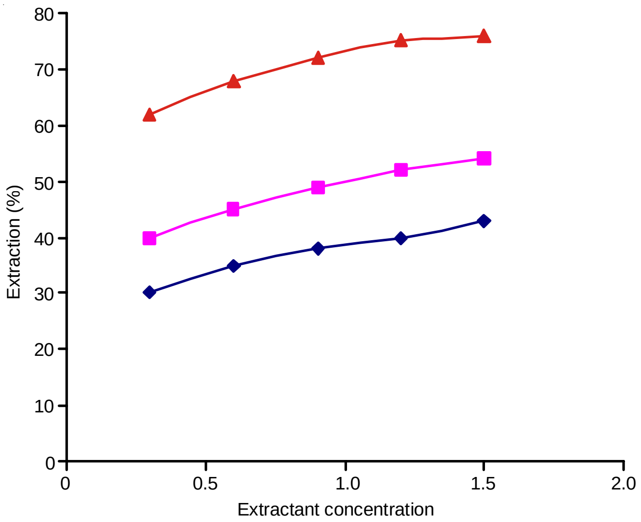

Fig. 3. Effect of extractant (DBSO + Cyanex-272) on the extraction of Eu(III) from synergic mixture of 1 M DBSO-Cyanex-272 in chloroform

Influence of temperature on the europium extraction: The temperature variation effect ranging from 25-50 °C on the per cent extraction of europium with 1 M synergic mixture of DBSO and Cyanex-272 in chloroform from buffer solution of pH 3 was studied under previously optimized conditions and results are recorded in Fig. 4. These results showed that per cent extraction of europium decreased with increasing temperature in the range studied. This suggests that temperature has inverse effect on the extraction of europium because the formation of extractable species is an exothermic process. Therefore, low temperature favors the extraction of europium in the proposed extraction system.

Effect of metal ion concentration: The effect of metal ion concentration on its extraction with 1 M synergic mixture of DBSO and Cyanex-272 in chloroform from buffer solution of PH 3 has been investigated (Table-1). The concentration of europium ranging from 6.6×10^{-4} to 6.58×10^{-3} mol/dm^3 was studied for this purpose. Other parameters were kept constant under optimized conditions. This shows that extraction increases with increasing metal ion concentration. An increase in per cent

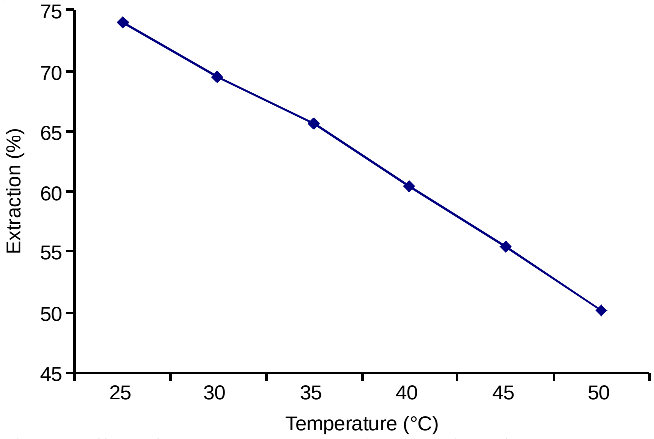

Fig. 4. Effect of temperature (°C) on the extraction of Eu(III) using a synergic mixture of 1 M DBSO-Cyanex-272 in chloroform

TABLE-1
INFLUENCE OF METAL IONS CONCENTRATION ON THE EXTRACTION OF Eu(III) FROM BUFFER SOLUTION pH 3 WITH 1 M SYNERGIC MIXTURE OF DBSO-CYANEX-272 IN CHLOROFORM

[Eu] (mol/dm^3)	Extraction (%)	[Eu] (mol/dm^3)	Extraction (%)
6.6×10^{-4}	74	3.94×10^{-3}	76
1.31×10^{-3}	74	4.60×10^{-3}	77
1.97×10^{-3}	74	5.26×10^{-3}	76
2.63×10^{-3}	75	5.92×10^{-3}	76
3.29×10^{-3}	76	6.58×10^{-3}	75

extraction of europium with increasing metal ion concentration indicates that proposed extraction system has high loading potential which is very encouraging and practicable for exploitation of metal on industrial scale.

Effect of cations on the extraction: The effect of various cations on the extraction of europium with 1 M synergic mixture of DBSO and Cyanex-272 in chloroform from buffer solution was examined. All other parameters were kept constant under previously optimized conditions. In general, the cations were added as their nitrate and chloride salts (about 10 mg/cm^3). The results are listed in Table-2. Among the cations studied Ni(II), Ba(II), Pb(II), Sr(II), Fe(III), Cu(II) and Co(II) slightly reduced the extraction (4-6 %) of europium whereas all other cations studied have no significant effect on the extraction. These cations may absorb in the same region of metal complex under study.

Effect of anions on the extraction: Various anions (about 10 mg/cm^3) as their sodium and potassium salts were used for their effect on the extraction of europium with 1 M synergic mixture of DBSO and Cyanex-272 in chloroform under previously optimized conditions. Results are presented in Table-3. The data indicate that PO_4^{3-}, SO_4^{2-}, Cl^-, Br^-, F^-, $C_2O_4^{2-}$ and $S_2O_3^{2-}$ masked the Eu(III) ions. These anions form stable complexes with europium prior to its extraction due to their higher formation constants with europium. Among others, citrate, cyanide, acetate and sulphide have shown slightly adverse effect on the extraction of Eu(III). The proposed synergistic mixture is proved to be much less sensitive to such interference while extracting Eu(III).

TABLE-2
EFFECT OF COMMON CATIONS ON THE EXTRACTION OF Eu(III) FROM BUFFER SOLUTION OF pH 3 WITH 1 M SYNERGIC MIXTURE OF DBSO-CYANEX-272 IN CHLOROFORM

Cations added (10 mg/mL)	Extraction (%)	± Deviation (from normal values)
Nil	74	Nil
Fe(III)	71	-4.0
Cu(II)	72	-2.7
Ni (II)	69	-6.7
Co(II)	72	-2.7
Zn(II)	73	-1.4
Sr(II)	70	-5.4
Ba(II)	69.2	-6.5
Mg(II)	73.2	-1.1
Al(III)	74.1	0.1
Pb(II)	72.9	-2.2
Na(I)	73.9	-0.2
K(I)	73.9	-0.2

TABLE-3
EFFECT OF COMMON ANIONS ON THE EXTRACTION OF EUROPIUM FROM BUFFER SOLUTION (pH 3) WITH 1 M SYNERGIC MIXTURE OF DBSO-CYANEX-272 IN CHLOROFORM

Anions added (10 mg/mL)	Extraction (%)	± Deviation (from normal values)
Nil	74	Nil
Fluoride	70	-5.4
Citrate	72	-2.7
Oxalate	71	-4.5
Cyanide	72	-2.7
Acetate	73	-1.4
Thiosulphate	71	-4.5
Phosphate	26.5	-62
Chloride	71.1	-5.4
Sulphate	68.5	-10.1
Sulphide	72.5	-2.2
Bromide	71	-4.5

Effect of salting-out agent on extraction of Eu(III): The effect of aluminum nitrate as salting-out agent on the extraction of europium with 1 M synergic mixture of DBSO and Cyanex-272 in chloroform from buffer solution was examined by keeping all other parameters constant under previously optimized conditions. The results are listed in Table-4 indicated a slight increase in the per cent extraction of europium with increasing nitrate concentration (10-150 mg/3 mL). This shows that salting out agent has no pronounced effect on the extraction of europium in the system reported herein.

TABLE-4
INFLUENCE OF SALTING OUT AGENT (ALUMINUM NITRATE) ON THE EXTRACTION OF EUROPIUM FROM BUFFER SOLUTION (pH 3) WITH 1 M SYNERGIC MIXTURE OF DBSO-CYANEX-272 IN CHLOROFORM

Salting out agent [$Al(NO_3)_3$] (mg/3 mL)	Extraction (%)
Nil	74.0
10	74.3
30	77.2
50	77.5
100	77.8
130	79.0
150	79.0

Study of stripping agents: The stripping investigations were observed to select appropriate strip solutions for the extraction of Eu(III) using 1 M synergic mixture of DBSO-

Cyanex-272 in chloroform. Nitric acid (0.1 M), ammonium hydroxide (0.1 M) solutions along with deionized water were used as strippants respectively. The results are represented in Table-5. Ammonium hydroxide (0.1 M) was found to be the most effective phase with equal volume ensures 90 % recovery of europium in two steps. The recovery of europium with distilled water was found to be 89 % whereas the recovery of europium with (0.1 M) HNO_3 was only 75 %. Deionized water was finally chosen as stripping agent for europium back extraction due to its economical suitability, easy handling and comparatively good refining of europium from organic phase.

TABLE-5
STUDY OF VARIOUS STRIPPING AGENTS FOR THE RECOVERY OF Eu(III) FROM BUFFER SOLUTION pH 3 WITH 1 M SYNERGIC MIXTURE OF DBSO-CYANEX-272 IN CHLOROFORM

Strippant	1st Stage (%)	2nd Stage (%)	3rd Stage (%)	Total recovery (%)
0.1 M NH_4OH	75	14	2.5	92
Distilled water	70	19	2.0	89
0.1 M HNO_3	56	20	1.0	75

Recycling of extractants: The ability of synergic mixture (DBSO and Cyanex-272 in chloroform) to be recycled for the extraction of europium was investigated. The results are shown in Table-6. The extracting ability of the organic extractants for europium extraction was checked four times by repeating the same solvent and found to be efficient and stable with almost same extractability.

TABLE-6
RECYCLING OF EXTRACTING MATERIAL (DBSO-CYANEX-272 IN CHLOROFORM)

No. of cycles	Extraction (%)
1	74
2	70
3	65
4	60

Accuracy of the extraction procedure: The accuracy of the extraction method reported herein has been checked by extracting europium contents (100-4000 ppm) from its standard solutions. Results are presented in Table-7 show that the per cent deviation decreases with increasing metal ion concentration. It was further noted that loading capacity of DBSO and Cyanex-272 for europium is quite high to extract the metal ions present in the concentration range studied. Decrease in per cent deviation at high metal ion concentration may be due to the fluctuations caused by dilution at spectrophotometric determination step. The decrease in per cent deviation at higher metal ion concentration may be due to the fact that competition of aqueous phase for organic phase get decreased and maximum extraction occurs which causes an appreciable decrease in the expected error. Therefore, better results can be achieved by using an appropriate concentration of metal ions in this extraction system.

Conclusion

In this method, quantitative extraction of Eu(III) from buffer solution of pH 3 can be achieved by using 1 M synergic mixture of DBSO and Cyanex-272 in chloroform. More than 90 % extracted europium can be stripped back using deionized water in three stages. A clean separation of europium from associated elements in its local ores is possible. The process is economical due to selective extraction, stability and low cost of extractants (DBSO and Cyanex-272). The reported work is both economical and new. This can be used for reported metals on industrial scale. Most of the interfering anions and cations have been removed in the reported method. The solvent system used is commercially available.

TABLE-7
STUDY OF THE ACCURACY & PRECISION OF DEVELOPED Eu(III) FROM BUFFER SOLUTION pH 3 WITH 1 M SYNERGIC MIXTURE OF DBSO-CYANEX-272 IN CHLOROFORM

Europium added (ppm)	Europium found (ppm)	± Deviation (%)
100	50	-50
1000	870	-13
2000	1400	-30
3000	1900	-36.6
4000	2996	-0.09

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