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Solvent extraction of europium (III) with 4-thiobenzoyl 2,4-dihydro 5-methyl 2-phenyl 3H-pyrazol-3-one (SBMPP) and thiobenzoyltrifluoroacetone (SBTA)

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Abstract. Thio derivatives of 4-benzoyl 2,4-dihydro 5-methyl 2-phenyl 3H-pyrazol-3-one (SBMPP) and benzoyltrifluoroacetone (SBTA) have been employed as extractants for the extraction of europium (III). Europium (III) was extracted from buffered aqueous media into benzene as Eu $(SBMPP)_3$ and Eu $(SBTA)_3$ chelates. The effect of phosphorus esters, tri-octylphosphine oxide (TOPO) and tributylphosphate (TBP) and hetero cyclic bases, pyridine, γ-picoline and quinoline as auxiliary ligands on the extraction of europium (III) was studied. A large synergistic enhancement was observed in all systems. The values of equilibrium constants (log K_{ex}) and adduct formation constants (log K_s) have been calculated.

Keywords. Synergistic extraction ; thiobenzoyl trifluoroacetone ; extraction constant ; adduct formation constant ; europium.

1. Introduction

Extraction of metals by 4-acylpyrazolones, especially 4-benzoyl 2,4-dihydro 5-methyl 2-phenyl 3H-pyrazol-3-one (BMPP), with or without addition of synergists has been reviewed (Nageswara Rao and Thakur 1975). Since BMPP is better than TTA in the extraction of many metals it is expected that 4-thiobenzoyl 2,4-dihydro 5-methyl 2-phenyl 3H-pyrazol-3-one (SBMPP) would be a better ligand than thiothenoyltrifluoroacetone (STTA). Benzoyltrifluoroacetone (BTA) has lower pKa value than TTA (Shukla *et al* 1974) and it extracts cobalt (II) at lower pH compared to TTA (Wang and Li 1977). So it was considered interesting to prepare the thioderivative of BTA and use for the extraction of europium (III). Our previous studies with SBMPP (Chouhan and Rao 1979) and thiobenzoyltrifluoroacetone (SBTA) (Rao and Chouhan 1979, 1980) showed that these thioligands extract cobalt (II) and zinc (II) at lower pH values than their parent compounds, i.e., BMPP and BTA respectively.

The aim of the present work is to compare the efficiency of SBMPP and SBTA in the extraction of a lanthanide, namely, europium (III), with BMPP and BTA.

The effect of various types of organic lewis bases as auxiliary ligands on the extraction of europium (III) with SBMPP and SBTA was investigated. Phosphorous esters, tri-*n*-octylphosphine oxide (TOPO) and tri-*n*-butylphosphate (TBP) were selected as oxygen containing lewis basis and heterocyclic N-bases pyridine, γ-picoline and quinoline as nitrogen containing lewis bases.

2. Experimental

Though 4-benzoyl 2,4-dihydro 5-methyl 2-phenyl 3H-pyrazol-3-one (BMPP) is not commercially available, it can be prepared according to the method of Jensen (1959) by making use of 2,4-dihydro 5-methyl 2-phenyl 3H-pyrazol-3-one (MPP) and benzoylchloride. Thioderivatives of BMPP and BTA have been prepared by adopting a method similar to that employed by Berg and Reed (1966) for the synthesis of thioderivatives of β-diketones. Both compounds were purified by recrystallisation twice from absolute alcohol. The purity of SBMPP and SBTA was established by microanalysis for carbon, hydrogen and nitrogen. Molecular weights of SBMPP and SBTA, determined cryoscopically in benzene solution, were 296 and 234 (cald. Mol. wt. SBMPP = 294, SBTA = 232) respectively. In 70/30 (V/V) dioxane water medium pKa values of SBMPP, (BMPP = 5·72) and SBTA (BTA = 6·88) were found to be 5·46 and 6·16 respectively. These thioligands were stored in a refrigerator. All the chemicals used were of standard reagent grade A radioisotope$^{152+154}$ europium (Specific activity = 3 mci) obtained from Bhabha Atomic Research Centre, Bombay, was used as radiotracer. This solution was diluted 1,00,000 times for the actual work and γ-energy at 0·125 MeV was measured.

A NaI (Tl) well-type scintillation counter (ECL, India) was used for counting the γ-activity of the isotope. Measurements of pH were made using expanded scale pH meter (ECL, India). A wrist type of mechanical shaker was used for shaking.

Solvent extraction of europium (III) from buffered (acetate buffers) aqueous medium into benzene containing one millimolar ligand (SBMPP or SBTA) with and without lewis bases was carried out by the usual methods. All the experiments were performed at 26 ± 1° C and the ionic strength of the aqueous phase was maintained at 0·1 M. Distribution ratio (K_d) was obtained by measuring the γ-activity of both phases after extraction.

3. Results and discussion

The slope value of the plot of log K_d (distribution ratio) against pH at constant ligand concentration (10^{-3} M) is three in Eu(III)–SBMPP system indicating that three protons are released during the extraction process. A plot of log K_d against log (ligand) at constant pH also gives a slope of 3 ± 0·1 (figure 1) indicating that three moles of ligand are required for the formation of extractable species. Hence the extraction equilibrium can be represented as

$$Eu^{3+} + 3HA \overset{K_{ex}}{\rightleftharpoons} EuA_3 + 3H^+, \quad (1)$$

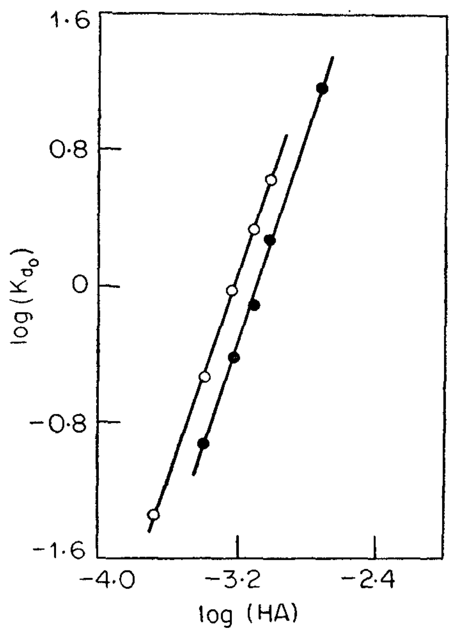

Figure 1. Plot of log K_{d_0} vs log (HA)—Europium (III)-SBMPP system, pH = 5·58 —Europium (III)-SBTA system, pH = 6·86.

where HA represents the ligand (SBMPP) and K_{ex} is equilibrium constant. Similar results were obtained in Eu(III)-SBTA system. The value of equilibrium constant (log K_{ex}) has been calculated by using the equation

$$\log K_{ex} = \log K_d - 3\text{pH} - 3 \log(\text{HA}). \tag{2}$$

The log K_{ex} values obtained were −7·08 and −11·34 for Eu(III)-SBMPP and Eu(III)-SBTA system respectively. The corresponding values for Eu(III)-TTA (Sekine and Dyrssen 1967), Eu(III)-SBMPP (Chmutova and Kochetkova 1969) and Eu(III)-BTA (Chouhan 1978) systems are −11·68, −3·96 and −9·72. Thus, thioligands SBMPP and SBTA are inferior to their respective parent compounds, BMPP and BTA for the extraction of europium (III) whereas for the extraction of cobalt (II) and zinc (II) reverse is the case (Chouhan and Rao 1979; Rao and Chouhan 1979, 1981). Similar results have been reported (Nag and Choudhury 1976) for the extraction of neodymium (III) with STTA. This type of behaviour of thioligands for the extraction of europium (III), can be explained on the basis of hard and soft acid and base theory. Thioligands are soft bases due to the presence of soft donor atom-like sulphur but europium (III) is a typical hard acid, which does not form strong complexes with soft chelating ligands.

The effect of lewis bases (S) in combination with ligands (SBMPP and SBTA) on the extraction of europium (III) was studied by varying the concentration of lewis bases at constant ligand concentration and pH. This type of study gives information about the number of auxiliary ligands incorporated in the adduct formation. Experiments conducted at constant auxiliary ligand concentration and pH with varying concentration of ligand, give information regarding the number of ligand molecules involved during the extraction process in the presence of auxiliary ligands. From the data obtained in the present study, extraction equilibrium for the extraction of europium (III) in the presence of auxiliary ligands may be represented as

$$\mathrm{Eu(III)} + 3\mathrm{HA} + xS \overset{K'_{ex}}{\rightleftharpoons} \mathrm{EuA_3}\,S_x + 3\mathrm{H}^+. \qquad (3)$$

The values of K'_{ex} have been calculated. Adduct stability constants and values of K'_{ex} are given in table 1.

3. 1. *Eu(III)–SBMPP–S system*

Figure 2 shows the plots of log K_d against log (S) at constant pH (2·74, 4·20, 5·15, 4·80 and 5·00 respectively for TOPO, TBP, pyridine, γ-picoline and quinoline) and constant ligand concentration (10^{-3} M or SBMPP) in benzene. Two molecules of TOPO, TBP and γ-picoline take part in adduct formation as indicated by the slope value of two, while pyridine and quinoline form adducts of the type Eu $(SBMPP)_3$ pyridine and $Eu(SBMPP)_3$ quinoline.

3.2. *Eu(III)–SBTA—S system*

The slope value of the plots of log K_d against log (S) (figure 3) at constant pH (TOPO = 4·14, TBP = 5·70, pyridine = 4·46, γ-picoline = 6·36 and quinoline = 6 .76) and constant SBTA (10^{-3} M) concentration is two for TOPO, TBP, γ-picoline and pyridine. The plot for quinoline has a slope of unity indicating that the extracted species is of the type $Eu(SBTA)_3$ quinoline.

Our results clearly indicate that synergistic enhancement of extraction occurs in these systems. In oxygen containing lewis bases TOPO is better than TBP as synergist, probably due to the higher basicity of TOPO as compared to TBP. Among nitrogen containing lewis bases γ-picoline exhibited more enhancement than pyridine and quinoline, in both the systems. Superiority of TOPO over

Table 1. Extraction constants of SBMPP and SBTA complexes of europium(III) and adduct formation constants.

Auxiliary Ligand	Eu(III)–SBMPP		Eu(III)–SBTA	
	Log K_{ex}'	Log K_s	Log K'_{ex}	Log K_s
Tri-n-octylphosphine oxide (TOPO)	4·78	11·86	0·94	12·28
Tri-n-butylphosphate (TBP)	0·64	7·72	−3·92	7·42
Pyridine	−0·18	2·90	−6·68	4·66
γ-picoline	−1·46	2·62	−6·08	5·26
Quinoline	−3·70	3·38	−8·36	2·48
..	−7·08	..	−11·34	..

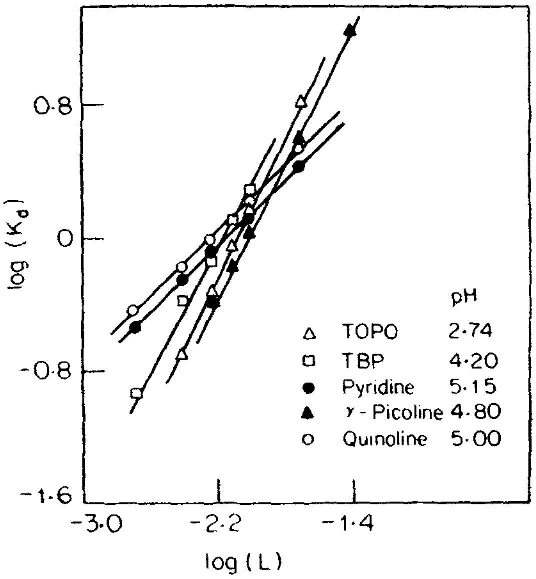

Figure 2. Plot of log K_d vs log (L), SBMPP $= 10^{-3}$ M in benzene.

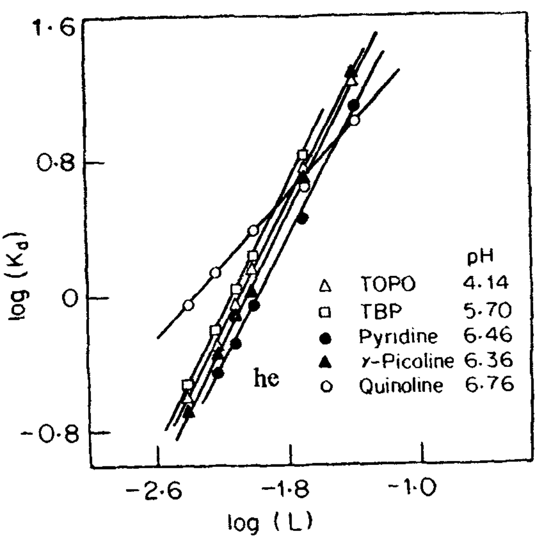

Figure 3. Plot of log K_d vs log (L). SBTA $=10^{-3}$ M in benzene.

TBP and γ-picoline over pyridine and quinoline has been reported earlier in literature. We have also observed similar synergistic effect of these lewis bases on the extraction of cobalt (II) and zinc (II) with SBMPP and SBTA (Chouhan 1978).

In the presence of TOPO adduct formation constant is smaller with europium(III) benzoyltrifluoroacetonate (log K_s = 10·52) (Chouhan 1978), log $\beta_2 = 11 \cdot 70$

(Shigematsu *et al* 1967) than europium(III) thiobenzoyl trifluoroacetonate (log K_s = 12·28). Since the extraction constant of europium (III) benzoyltrifluoroacetonate (log K_{ex} = − 9·72) is higher than that of europium (III) thiobenzoyltrifluoroacetonate (log K_{ex} = −11·34), the general idea (Honjo and Shigematsu 1968) that as the extraction constant of the chelate increases, the stability constant of the adduct decreases also holds good in the present work.

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References

Berg E W and Reed K P 1966 *Anal. Chim. Acta* **36** 372
Chmutova M K and Kochetkova N E 1969 *Zh. Anal. Khim.* **24** 1757
Chouhan V S 1978 Solvent extraction of Cobalt (II), zinc (II) and europium (III) with thioderivatives of acylphyrazolones and β-diketones Ph.D. Thesis, Indian Institute of Technology, New Delhi
Chouhan V S and Rao G N 1979 *J. Radioanal. Chem.* **52** 199
Honjo T and Shigematsu T 1968 *Kagaku (Zasshi)* **23** 709
Jensen B S 1959 *Acta Chem. Scand* **13** 1668, 1890
Nag K and Chaudhury M 1976 *J. Inorg. Nucl. Chem.* **38** 309
Nageswara Rao G and Thakur J S 1975 *J. Sci. Ind. Res.* **34** 110
Rao G N and Chouhan V S 1979 *Indian J. Chem.* **A17** 154
Rao G N and Chouhan V S 1981 *J. Inorg. Nucl. Chem.* (in press)
Sekine T and Dyrssen D 1967 *J. Inorg. Nucl. Chem.* **29** 1457
Shigematsu T, Tabushi M, Matsui M and Honjyo T 1967 *Bull. Chem. Soc. Jpn.* **40** 2807
Shukla J P, Manchanda V K and Subramanian M S 1974 *J. Electroanal Chem.* **50** 253
Wang S M and Li N C 1967 *Solvent extraction chemistry* (Amsterdam : North Holland Publishing Company).