

Synergistic extraction of erbium(III) with 1-phenyl-3-methyl-4-*p*-nitrobenzoyl-5-pyrazolone and 3-phenyl-4-benzoyl-5-isoxazolone using neutral oxodons

P N Bangroo & H C Arora*

Department of Atomic Energy, Atomic Minerals Division, West Block-7, R.K. Puram, New Delhi 110 066

and

G N Rao & C R Jagga

Indian Institute of Technology, New Delhi 110 016

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Two different types of β -diketones, 1-phenyl-3-methyl-4-*p*-nitrobenzoyl-5-pyrazolone (NMPP) and 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) have been employed for the solvent extraction of erbium(III) from aqueous buffer media into toluene. The value of $\log K_{ex}$, where K_{ex} refers to the equilibrium, $Er(III) + 3HL \rightleftharpoons ErL_3 + 3H^+$ is -1.1 and $+0.9$ for Er-NMPP and Er-HPBI respectively. The effect of various lewis bases, viz., tri-*n*-octyl-phosphine oxide (TOPO), tri-*n*-butyl phosphate (TBP) and dibenzyl sulphoxide (DBSO) in combination with NMPP and HPBI respectively on the extraction of Er(III) has also been studied. A large synergistic enhancement has been observed in both the cases with all the lewis bases. Synergistic extraction constants, stability constants, and the stoichiometry of the respective adducts formed during the extraction have been determined.

Among the various chelating ligands used in solvent extraction of metals, β -diketones have been used extensively¹. 4-Acylpyrazolones, first introduced by Jensen², have proved to be the most promising reagents for the extraction of metals. Among these, 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (BMPP) has been found to be most successful reagent and is more efficient than theonyltrifluoroacetone (TTA) in most of the cases³. The introduction of the nitro group is expected to lower the pK_a value and thus the extraction may occur at lower *pH* values than that with its parent compound, BMPP. The reagent 1-phenyl-3-methyl-4-*p*-nitrobenzoyl-5-pyrazolone (NMPP) has been used earlier for the extraction of Cu, Co, Ni, Th³, UO₂^{4,5}, Nd and Eu⁶.

Replacement of the pyrazole moiety by isoxazole moiety in BMPP is expected to decrease its pK_a and facilitate extraction of metals at lower *pH* values. The reagent 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) has been used earlier for the extraction of Mn, Fe, Co, Ni, Zn, Cd, Pb, Rh⁷, Nd and Eu⁸.

The aim of the present work is to study the extraction of Er(III) as a member of the heavier rare earths with NMPP, HPBI, BMPP and TTA and compare their relative efficiencies. The effect of various organic lewis bases, i.e., tri-*n*-octylphosphine oxide (TOPO), tri-*n*-butyl phosphate (TBP) and dibenzyl sulphoxide (DBSO) on the extraction of Er(III) in combination with NMPP and HPBI has also been investigated.

Experimental

The ligand NMPP was prepared using 1-phenyl-3-methyl-5-pyrazolone (MPP) and *p*-nitrobenzoyl chloride by the method of Jensen². HPBI was prepared according to the method of Korte and Storiko⁹ using 3-phenyl-5-isoxazolone¹⁰ and benzoic anhydride in the presence of sodium benzoate. The purity of both the reagents was established by elemental analysis and melting point data. The solutions of NMPP and HPBI of requisite concentrations were prepared in toluene (AR).

Solution of Er(III) was prepared using the reagent grade Er₂O₃ (99.9% Koch-Light Labs, England) and stock solution was standardised gravimetrically after precipitation as oxalate. All other reagents were of AR grade.

Solvent extraction

The initial concentration of Er(III) in aqueous phase was maintained at $2.99 \times 10^{-4} M$ and the ionic strength was kept at $0.1 M$ (H,K)Cl. *pH* of aqueous phase was measured after the extraction in all the experiments using an Elico *pH* meter. Equal volumes (10 cm³) of pre-contacted aqueous phase and toluene phase containing the ligand NMPP were placed in stoppered pyrex glass bottles and shaken for one hour in a thermostated mechanical shaker at $30 \pm 1^\circ C$. The distribution ratio K_d was calculated by monitoring the concentration of Er(III) in the aqueous phase spectrophotometrically by developing colour with Alizarin Red-S¹¹ using a Varian-634 spectrophotometer. Since the K_d is found by ratio of the concentration of metal obtained by difference, the experiments were carried out in duplicate. Similar experiments were carried out to extract Er(III) with NMPP in combination with neutral oxo-donors TOPO, TBP and DBSO and the distribution ratios were calculated. All the above experiments were also carried out with the ligand HPBI.

Results and discussion

The extraction behaviour of Er(III) with NMPP and HPBI can be understood in terms of the variation of K_d as a function of the aqueous phase acidity and as a function of the extractant concentration. The plot of $\log K_d$ vs pH at constant ligand concentration (NMPP or HPBI) gave a slope of three for Er(III), indicating that three protons are released during extraction. The slope value of the plot of $\log K_d$ vs \log (NMPP) or \log (HPBI) at constant pH was also found to be 3 ± 0.1 indicating that three moles of the ligand NMPP (or HPBI) are involved in the formation of extracted complexes.

The extraction equilibrium can be represented as:

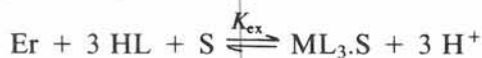
$$\text{Er(III)} + 3\text{HL} \xrightleftharpoons{K_{ex}} \text{ErL}_3 + 3\text{H}^+$$
 where HL represents the ligand NMPP or HPBI. The values of the equilibrium constant, $\log K_{ex}$, were calculated and are shown in Table 1, along with pK_a values of various ligands.

As the relative values of $\log K_{ex}$ under similar conditions provide an estimate of the relative efficiency of the extraction with various ligands, it is clear from Table 1 that both NMPP and HPBI are better extractants than BMPP and TTA. It is also evident that HPBI extracts Er(III) better than NMPP. This trend conforms to the pK_a values of various ligands, lower pK_a of the ligand signifying higher extraction.

Effect of lewis bases (S)

The effect of lewis bases in combination with the ligands NMPP/HPBI on the extraction of Er(III) was studied by varying the concentration of the lewis bases at constant pH and constant ligand concentration.

Figure 1 shows the plot of $\log K_d$ vs $\log(S)$ at constant pH and at constant NMPP concentration for Er(III) with TOPO, TBP and DBSO. The slopes indicate that 1 mole each of TOPO, TBP and DBSO takes part in the adduct formation. In the case of Er(III)-HPBI system also, one mole each of TOPO, TBP and DBSO is taken up for adduct formation (Fig. 2). From the data, the extraction equilibrium for the extraction of Er(III) in presence of auxillary ligands may be shown as:



where K_{ex} refers to the extraction equilibrium constant and is calculated by the equation:

$$\log K_{ex} = \log K_d - 3 \log[\text{HL}] - 3pH - \log[\text{S}]$$

The values of $\log K_{ex}$ and adduct stability constants ($\log K_s$) are given in Table 2.

Table 1—Comparison of extraction constant values ($\log K_{ex}$) of Er-NMPP and Er-HPBI systems with those for Er-BMPP and Er-TTA systems

System	pK_a	$\log K_{ex}$
Er-NMPP	2.0	-1.1 ^a
Er-HPBI	1.13 ^b	+0.9 ^b
Er-BMPP	4.10 ^b	-2.5
Er-TTA	6.23 ^b	-7.76 ^c

^a Present work; ^b Refs. 16 & 17; ^c Refs. 12,13,14 & 15.

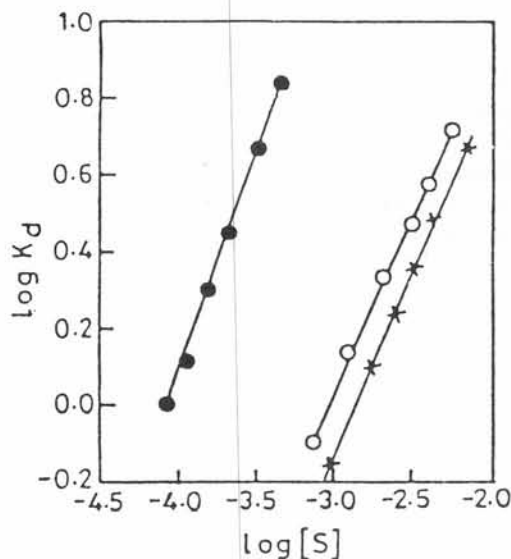


Fig. 1—Plot of $\log K_d$ vs $\log(S)$ [○ Er-NMPP-TBP, $pH = 2.3$; ● Er-NMPP-TOPO, $pH = 2.2$; and × Er-NMPP-DBSO, $pH = 2.1$. (NMPP) = 0.02 M in toluene]

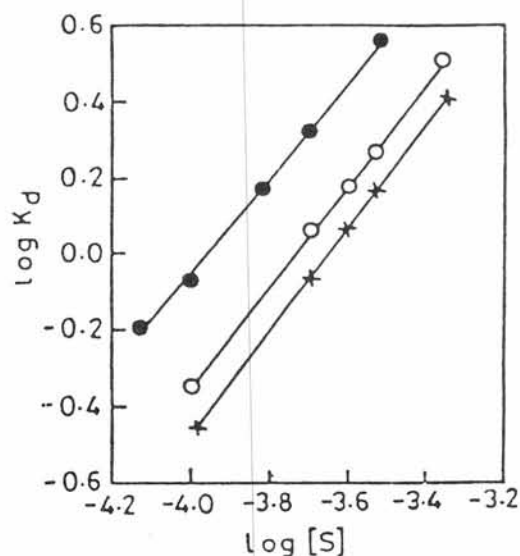


Fig. 2—Plot of $\log K_d$ vs $\log(S)$ [● Er-HPBI-TOPO, $pH = 1.9$; ○ Er-HPBI-TBP, $pH = 2.0$; and × Er-HPBI-DBSO, $pH = 2.0$. (HPBI) = 0.005 M in toluene]

Table 2—Extraction constants and stability constants of Er-NMPP-S and Er-HPBI-S adducts

Auxillary ligand	Er(III)-NMPP		Er(III)-HPBI	
	log K_{ex}	log K_s	log K_{ex}	log K_s
TOPO	2.6	3.7	5.1	4.2
TBP	1.5	2.6	4.8	3.9
DBSO	1.1	2.2	4.3	3.4
—	-1.1	—	+0.9	—

The results clearly indicate that synergistic enhancement occurs in these systems and the synergism with TOPO is higher than that with TBP and DBSO which is probably due to its higher basicity.

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