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

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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, $\text{Er}^{3+} + 3\text{HL} \leftrightarrow \text{ErL}_3 + 3\text{H}^+$ 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), 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 extensively$^1$. 4-Acylpyrazolones, first introduced by Jensen$^2$, have proved to be the most promising reagents for the extraction of metals. Among these, 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (BMP) has been found to be most successful reagent and is more efficient than theonyltrifluoroacetone (TTA) in most of the cases$^3$. 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, BMP. The reagent 1-phenyl-3-methyl-4-p-nitrobenzoyl-5-pyrazolone (NMPP) has been used earlier for the extraction of Cu, Co, Ni, Zn, Cd, Pb, Rh$^7$, Nd and Eu$^8$.

Replacement of the pyrazole moiety by isoxazole moiety in BMP has been expected to lower the $pK_a$ 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, Rh$^7$, Nd and Eu$^8$.

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, BMP 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 Jensen$^2$. HPBI was prepared according to the method of Korte and Storik$^9$ using 3-phenyl-5-isoxazolone$^{10}$ 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 $\text{Er}_2\text{O}_3$ (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 $2.99 \times 10^{-4} \text{M}$ 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 cm$^3$) of pre-contacted aqueous phase and toluene phase containing the ligand NMPP were placed in stoppered pyrex glass bottles shaken for one hour in a thermostated mechanical shaker at 30 ± 1°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-S$^{11}$ 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 $pH$ at constant ligand concentration (NMPP or HPBI) was also found to be $3 \pm 0.1$ 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:

$$\text{Er(III)} + 3\text{HL} \rightleftharpoons \text{ErL}_3 + 3\text{H}^+$$

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 TOP, TBP and DBSO. The slopes indicate that 1 mole each of TOP, TBP and DBSO takes part in the adduct formation. In the case of Er(III)-HPBI system also, one mole each of TOP, 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 auxiliary ligands may be shown as:

$$\text{Er} + 3\text{HL} + S \rightleftharpoons \text{ML}_3\cdot S + 3\text{H}^+$$

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

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

The values of $\log K_{ex}$ and adduct stability constants ($\log K_d$) are given in Table 2.
Table 2—Extraction constants and stability constants of Er-NMPP-S and Er-HPBI-S adducts

<table>
<thead>
<tr>
<th>Auxiliary ligand</th>
<th>Er(III)-NMPP</th>
<th>Er(III)-HPBI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>log $K_{ex}$</td>
<td>log $K_s$</td>
</tr>
<tr>
<td>TOPO</td>
<td>2.6</td>
<td>3.7</td>
</tr>
<tr>
<td>TBP</td>
<td>1.5</td>
<td>2.6</td>
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<tr>
<td>DBSO</td>
<td>1.1</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>-1.1</td>
<td>-</td>
</tr>
</tbody>
</table>

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.

References
17 Marcus Y & Keretes A S, Ion exchange and solvent extraction of metal complexes (Wiley Interscience, New York) 1967.