Chapter 5

Steric effects of Polymethylene Chain of 4-Acylbis(pyrazolones) on the Solvent Extraction of Trivalent Lanthanoids: Synergistic effect with Mono and Bifunctional Neutral Organophosphorus Extractants
A large number of acidic and neutral organophosphorus extractants have been widely employed industrially for the solvent extraction separation of lanthanoids [Bautista 1995; Powell 1979]. However, these reagents display various shortcomings such as poor selectivity, third phase formation etc. [Reddy et al. 1995]. Thus, there is a growing interest in the development of new and more selective solvent extraction reagents for the extraction and separation of trivalent lanthanoids in view of the ever-increasing demand for high purity lanthanoid elements, individually and collectively.

1-Phenyl-3-methyl-4-acyl-5-pyrazolones (A) are well known heterocyclic β-diketone type chelating ligands coordinating to the metal ion with oxygen atoms as "hard" Lewis bases.

Further, these ligands have a strong affinity towards "hard" Lewis acids like lanthanoids [Umetani et al. 2000; Bond et al. 2000].

A 4-acylbis(pyrazolone) (B) designed by combining two 1-phenyl-3-methyl-4-acyl-5-pyrazolone subunits linked by a polymethylene chain of
varying lengths -(CH$_2$)$_n$ (n = 0-8, 10, 20) exhibit several unique properties such as larger partition coefficients than the parent 4-acyl-5-pyrazolone and has two β-diketone donor sites on both sides of the polymethylene chain, is expected to give specific complexation towards metal ions depending on the polymethylene chain length. The dependence of the polymethylene chain length of 4-acylbis(pyrazolone) on the extraction behavior of Cu$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Am$^{3+}$, Cm$^{3+}$, Cr$^{3+}$, UO$_2^{2+}$, Th$^{4+}$, Np$^{4+}$ and Pu$^{4+}$ has been well documented [Miyazaki et al. 1989; Miyazaki et al. 1991; Reddy et al. 2000; Takeishi et al. 2001].

A synergistic effect is often set to bring about enhanced extraction but poorer separation among the metal ions. However, interestingly, in the extraction of Zn$^{2+}$ and Ni$^{2+}$ with 4-acylbis(pyrazolones), an enhanced extraction and an improved separation have been reported in the presence of TOPO as a synergist [Miyazaki et al. 1991]. The above factors prompted us to synthesize various derivatives of 4-acylbis(pyrazolones) of varying polymethylene chain length and investigate their extraction behavior with Ln$^{3+}$ ions. The orientation and steric effects of the polymethylene substituent were examined by semi-empirical PM3 molecular modeling calculations. Further, the effect of addition of various mono- (TOPO and
TBP) and bifunctional (CMPO) organophosphorus extractants on the extraction of Ln$^{3+}$ ions with 4-acyl bis(pyrazolone) has also been evaluated.

\[
\begin{align*}
\text{TOPO} & : \quad \text{H}_2\text{C}(\text{H}_2\text{C})_7\text{P}-(\text{CH}_2)_7\text{CH}_3 \\
\text{TBP} & : \quad \text{H}_3\text{C}(\text{H}_2\text{C})_3\text{O}P\text{O}(\text{CH}_2)_3\text{CH}_3 \\
\text{CMPO} & : \quad \text{C}_8\text{H}_{17}\text{P}N(\text{CH}_2\text{CHCH}_3)_2
\end{align*}
\]

5.1. Experimental

5.1.1. Instrumentation

A Hitachi (Tokyo, Japan) 220 double-beam microprocessor-controlled spectrophotometer was used for measuring absorbance. $^{31}$P NMR spectra of the synergistic complexes (in CDCl$_3$ and 85% H$_3$PO$_4$ as an external standard) were recorded using a Bruker 121.47 MHz NMR spectrometer. The methods for the preparation of stock solutions of Ln$^{3+}$ ions and other instruments employed in this chapter are the same as described in chapter 3.
5.1.2. Materials

TBP, TOPO and the starting materials (1-phenyl-3-methyl-5-pyrazolone and various acid dichlorides) for the syntheses of ligands were obtained from Sigma-Aldrich. CMPO was synthesised and purified by standard procedures [Mathur et al. 1992; Gatrone et al. 1987]. All the other chemicals used were of analytical reagent grade.

Syntheses of ligands:

Various 4-acylbis(pyrazolones) were prepared by the acylation of 1-phenyl-3-methyl-5-pyrazolone with the corresponding acid dichloride [Jensen 1959] (Scheme 5.1).

The crude compounds were recrystallized from chloroform-hexane mixture and dried under reduced pressure. The purity of the compounds was
established by elemental analyses, IR and $^1$H NMR spectral data (Figs. 5.1-5.4).

4-Adipoylbis(1-phenyl-3-methyl-5-pyrazolone) (H$_2$AdBP): M.P. 199°C; Elemental analysis: Calc. for C$_{26}$H$_{26}$O$_4$N$_4$: C, 68.12; H, 5.68; N, 12.23. Found C, 68.27; H, 6.19; N, 12.04 %; $^1$H NMR data (CDCl$_3$/TMS): $\delta$ 7.80-7.83, 7.42-7.47, 7.28-7.31 (m, 10H, Ph); 2.80-2.83 (t, 4H, (CH$_2$)$_2$); 2.49 (s, 6H, CH$_3$); 1.88 (m, 4H, (CH$_2$)$_2$) (Fig. 5.1); IR (KBr) data ($\nu$ cm$^{-1}$): 3409 (br,OH); 1633 (s, C=O); 1593 (s, phenyl C=C); 1560 (s, pyrazolone ring).

![Fig. 5.1. $^1$H NMR spectrum of H$_2$AdBP.](image)

4-Suberoylbis(1-phenyl-3-methyl-5-pyrazolone) (H$_2$SuBP): M.P. 216°C; Elemental analysis: Calc. for C$_{28}$H$_{30}$O$_4$N$_4$: C, 69.13; H, 6.17; N, 11.53. Found C, 69.22; H, 6.43; N, 11.43 %; $^1$H NMR data (CDCl$_3$/TMS): $\delta$ 7.81-7.84, 7.42-7.47, 7.28-7.31 (m, 10H, Ph); 2.74-2.79 (t, 4H, (CH$_2$)$_2$); 2.48 (s, 6H, CH$_3$); 1.79 (m, 4H, (CH$_2$)$_2$); 1.49 (m, 4H, (CH$_2$)$_2$) (Fig. 5.2); IR (KBr) data ($\nu$ cm$^{-1}$): 3409 (br, OH); 1627 (s, C=O); 1596 (s, phenyl C=C); 1546 (s, pyrazolone ring).
Fig. 5.2. $^1$H NMR spectrum of H$_2$SuBP.

4-Sebacoylbis(1-phenyl-3-methyl-5-pyrazolone) (H$_2$SbBP): M.P. 136°C; Elemental analysis: calculated for C$_{30}$H$_{34}$O$_4$N$_4$: C, 70.03; H, 6.61; N, 10.89. Found C, 69.48; H, 6.51; N, 10.67 %. $^1$H NMR data (CDCl$_3$/TMS): $\delta$ 7.81-7.84, 7.42-7.47, 7.28-7.30 (m, 10H, Ph); 2.71-2.76 (t, 4H, (CH$_2$)$_2$); 2.48 (s, 6H, CH$_3$); 1.73-1.77 (m, 4H, (CH$_2$)$_2$); 1.39 (m, 8H, (CH$_2$)$_4$) (Fig. 5.3); IR (KBr) data (υ cm$^{-1}$): 3430 (br, OH); 1633 (s, C=O); 1593 (s, phenyl C=C); 1553 (s, pyrazolone ring).

4-Dodecandioylbis(1-phenyl-3-methyl-5-pyrazolone) (H$_2$DdBP): M.P. 152°C; Elemental analysis: calculated for C$_{32}$H$_{38}$O$_4$N$_4$: C, 70.84; H, 7.01; N, 10.33; Found C, 71.32; H, 7.45; N, 10.35 %. $^1$H NMR data (CDCl$_3$/TMS): $\delta$ 7.81-7.84, 7.42-7.47, 7.28-7.30 (m, 10H, Ph); 2.71-2.76 (t, 4H, (CH$_2$)$_2$); 2.48 (s, 6H, CH$_3$); 1.69-1.77 (m, 4H, (CH$_2$)$_2$); 1.33 (m, 12H, (CH$_2$)$_6$) (Fig. 5.4); IR (KBr) data (υ cm$^{-1}$): 3436 (br, OH); 1620 (s, C=O); 1593 (s, phenyl C=C); 1560 (s, pyrazolone ring).
5.1.3. Solvent extraction and analytical procedure

Equal volumes of aqueous (1.0 mol dm$^{-3}$ NaNO$_3$ and 1.0 × 10$^{-4}$ mol dm$^{-3}$ Ln$^{3+}$ ions) and organic phases were shaken at 303 ± 1 K for 60 min. Preliminary experiments showed that the extraction equilibrium was
attained within 15 min. The Ln$^{3+}$ ion in the aqueous phase was determined spectrophotometrically by Arsenazo-1 method [Snell 1978]. After allowing the phases to settle, 5.0 cm$^3$ aliquots of the aqueous phase were pipetted into a 25.0 cm$^3$ beaker and 1.0 cm$^3$ ammonium acetate (0.1 mol dm$^{-3}$) solution and 5.0 cm$^3$ Arsenazo 1 (0.01 %) solution were added. After adjusting the pH to 7.5, the solution was made up to 25.0 cm$^3$. The absorbances of the solutions were measured at 575 nm and the metal concentrations were computed from the respective calibration graphs. The Ln$^{3+}$ ion concentration in the organic phase was obtained by material balance. These concentrations were used to obtain the distribution ratio, $D$, defined as $D = [\text{Ln}^{3+}]_{\text{org}} / [\text{Ln}^{3+}]_{\text{aq}}$. All the experiments were performed in duplicate and the general agreement with $D$ values obtained was within ± 5%. The extracted complexes were deduced from the distribution data by both graphical and theoretical methods taking into account aqueous phase complexation of Ln$^{3+}$ ion with inorganic ligands and plausible complexes extracted into the organic phase.

5.2. Results and Discussion

5.2.1. Extraction of Ln$^{3+}$ ions with various 4-acylbis(pyrazolones)

The extraction behaviour of Nd$^{3+}$, Eu$^{3+}$ and Tm$^{3+}$ ions as a function of H$_2$SbBP concentration (0.01-0.03 mol dm$^{-3}$) was investigated from 1.0 mol dm$^{-3}$ NaNO$_3$ solutions of pH = 3.0 containing 1.0 $\times$ 10$^{-4}$ mol dm$^{-3}$ Ln$^{3+}$ ion as the aqueous phase and the results are depicted in Fig. 5.5. The extraction efficiency of Ln$^{3+}$ ion increases linearly with increasing concentration of H$_2$SbBP in the organic phase. Also the extraction efficiency increases monotonically with increase in the atomic number of
Ln$^{3+}$ ion. From the slopes of the log-log plot it is clear that two moles of H$_2$SbBP are involved in the extracted complexes. The effect of pH (2.75-3.06) on the extraction behaviour of Ln$^{3+}$ ion at constant H$_2$SbBP (0.02 mol dm$^{-3}$) shows an inverse dependence on acidity (Fig. 5.6).

![Log-log plot for Ln$^{3+}$ extraction](image)

Fig. 5.5. Effect of H$_2$SbBP concentration on the extraction of Ln$^{3+}$ ions.

![pH vs. Log D plot](image)

Fig. 5.6. Effect of pH on the extraction of Ln$^{3+}$ ions.

[[$H_2$SbBP]$=0.02$ mol dm$^{-3}$.]
A slope of 3.0 ± 0.1 observed in log $D$ vs. pH plot, indicates the release of three hydrogen ions by the interaction of $\text{Ln}^{3+}$ ion with two moles of $\text{H}_2\text{SbBP}$.

Based on the preceding studies, the extraction equilibrium involved in the extraction of $\text{Ln}^{3+}$ ions from dilute nitric acid solutions with 4-acylbis(pyrazolone) ($\text{H}_2\text{X}$) alone may be expressed as:

$$
\text{Ln}^{3+\text{aq}} + 2 \text{H}_2\text{X}_{\text{org}} \rightleftharpoons K_{\text{ex}} \text{Ln(X)(HX)}_{\text{org}} + 3 \text{H}^+_{\text{aq}} \tag{1}
$$

where $K_{\text{ex}}$ denotes the equilibrium constant.

$$
K_{\text{ex}} = \frac{[\text{Ln(X)(HX)}]_{\text{org}} [\text{H}^+]^3_{\text{aq}}}{[\text{Ln}^{3+}]_{\text{aq}} [\text{H}_2\text{X}]^2_{\text{org}}} \tag{2}
$$

$\text{Ln}^{3+}$ ions in the aqueous phase form a variety of complexes with nitrate ions. Then the total concentration of $\text{Ln}^{3+}$ ion ([Ln$^{3+}$]$_T$) in the aqueous phase can be expressed as:

$$
[\text{Ln}^{3+}]_T = [\text{Ln}^{3+}] + [\text{Ln(NO}_3)_{2+}] + [\text{Ln(NO}_3)_2^+] = [\text{Ln}^{3+}] (1 + \beta_1 [\text{NO}_3^-] + \beta_2 [\text{NO}_3^-]^2) \tag{3}
$$

where $\beta_1$ and $\beta_2$ are the stability constants [Smith and Martell 1976] of the following reactions:

$$
\text{Ln}^{3+} + \text{NO}_3^- \rightleftharpoons \beta_1 \text{Ln(NO}_3)_{2+} \tag{4}
$$

$$
\text{Ln}^{3+} + 2 \text{NO}_3^- \rightleftharpoons \beta_2 \text{Ln(NO}_3)_2^+ \tag{5}
$$

The distribution ratio, $D$, of $\text{Ln}^{3+}$ ion can be written from Eqs. (2) & (3) as:

$$
D = \frac{K_{\text{ex}} [\text{H}_2\text{X}]^2_{\text{org}}}{[\text{H}^+]^3 (1 + \beta_1 [\text{NO}_3^-] + \beta_2 [\text{NO}_3^-]^2)} \tag{6}
$$

The $K_{\text{ex}}$ values of the extracted complexes were determined by non-linear regression analysis with the aid of suitable chemically based model
developed taking into account the aqueous phase complexation of \( \text{Ln}^{3+} \) ion with inorganic ligands and all plausible complexes extracted into the organic phase using Eq. (6), as described in Chapter 3. The \( K_{\text{ex}} \) values thus calculated refer only to concentration quotients, calculated on the assumption that the activity coefficients of the species involved do not change significantly under the present experimental conditions. The log \( K_{\text{ex}} \) values of \( H_2\text{SbBP} \) (Log \( K_{\text{ex},\text{Nd}} = -5.64 \pm 0.04 \), Log \( K_{\text{ex},\text{Eu}} = -5.21 \pm 0.03 \) and Log \( K_{\text{ex},\text{Tm}} = -4.79 \pm 0.04 \)) increase with decreasing ionic radii of \( \text{Ln}^{3+} \) ion. In a polar diluent such as chloroform, this can be attributed to the increasing coulombic interactions with charge density of the \( \text{Ln}^{3+} \) ion [Manchanda et al. 1988]. The increase in the extractability across the \( \text{Ln}^{3+} \) series can be due to the increase in electrostatic interactions between the cation and the ligand with decrease in ionic radii. The trend observed in the present system is similar to that of various 4-acyl-5-pyrazolones [Umetani et al. 2000; Bond et al. 2000].

Fig. 5.7 shows the results on the effect of polymethylene chain length of bis(pyrazolone) on the extraction of \( \text{Eu}^{3+} \) ion. Solubility limitations and third phase formation have prevented the extraction studies with \( H_2\text{SuBP} \) \((n = 6)\). Extraction efficiency of \( \text{Eu}^{3+} \) ion increases with an increase in the number of \(-\text{CH}_2\)- groups from \( n = 4 \) to \( n = 8 \) and thereafter it decreases. This has been attributed to the increasing steric effect, caused by increasing polymethylene chain length from \( n = 8 \) to \( n = 10 \). The effect of hydrogen ion concentrations on the extraction of \( \text{Eu}^{3+} \) ion with various 4-acylbis(pyrazolones) has also been investigated and observed an inverse dependence on the acidity (Fig. 5.8). The Log \( K_{\text{ex}} \) values of \( \text{Eu}^{3+} \) ion with various 4-acylbis(pyrazolones) follow the order: \( H_2\text{SbBP} (-5.21 \pm 0.03) > H_2\text{AdBP} (-5.75 \pm 0.04) > H_2\text{DdBP} (-6.02 \pm 0.04) \). A similar trend has also
been observed in the extraction of trivalent actinides [Takeishi et al. 2001; Reddy et al. 2000].

Fig. 5.7. Effect of $[H_2X]$ on the extraction of Eu$^{3+}$ ion a: $H_2SbBP$, b: $H_2AdBP$ and c: $H_2DdB$.

Fig. 5.8. Effect of pH on the extraction of Eu$^{3+}$ ion a: $H_2SbBP$, b: $H_2AdBP$ and c: $H_2DdB$. 

Slope $= 2.0 \pm 0.1$

Slope $= 3.0 \pm 0.05$
In order to have a better understanding of the effect of polymethylene chain length on the extraction efficiency of Ln$^{3+}$ ion, semi-empirical PM3 molecular orbital calculations were carried out for 4-acyl bis(pyrazolones) by considering the H-bonding [Stewart 1989]. The keto-enol structures of various bis(pyrazolone) derivatives are shown in Fig. 5.9. The O---O distance (distance between the carbonyl oxygens connected to the polymethylene chain), thus calculated are correlated with the Log $K_{ex}$ values of Eu$^{3+}$ ion (Fig. 5.10). The Log $K_{ex}$ values increase to a maximum with increasing O---O distance up to 12.18 Å ($n = 8$) and then decreases for a distance $> 12.18$ Å.

Thus, a minimum distance of 12.18 Å between the carbonyl oxygens connected to the polymethylene chain, is required to achieve an optimal extraction of Ln$^{3+}$ ions. Further, for a distance greater than 12.18 Å, the decrease in the extraction efficiency of Ln$^{3+}$ ions may be due to steric factors. From the molecular modeling calculations, it can be concluded that the differences in the number of methylene groups and rigidity of these groups in the ligands, hence different steric effects and different orientations of the displaceable hydroxyl groups in the ligands are apparently the vital factors that govern the complexation of Ln$^{3+}$ ion.
Fig. 5.9. Keto-enol structures of 4-acyl bis(pyrazolones) suggested by molecular modeling: 1. H$_2$AdBP 2. H$_2$SuBP 3. H$_2$SbBP 4. H$_2$DdBP.
IR spectrum of the Eu\textsuperscript{3+}-H\textsubscript{2}SbBP binary complex shows a broad absorption in the region 3000-3500 cm\textsuperscript{-1} indicating the presence of water molecules in the complex (Fig. 5.11). The presence of water molecules in the extracted \(\beta\)-diketone complexes of Ln\textsuperscript{3+} ion is well documented [Mathur and Choppin 1993]. Further, strong bands due to \(\nu_{C=O}\), \(\nu_{C=N}\), and \(\nu_{C=C}\) of the aromatic rings were observed in the 1500-1650 cm\textsuperscript{-1} region, where the carbonyl band (1633 cm\textsuperscript{-1}) was shifted to lower frequency (1625 cm\textsuperscript{-1}), suggesting the involvement of oxygen of the carbonyl group in the complex formation with Eu\textsuperscript{3+} ion. The above results clearly show that Ln\textsuperscript{3+} ion is interacting with three of the \(\beta\)-diketone donor sites of the two H\textsubscript{2}SbBP molecules involved in the extraction process, releasing three H\textsuperscript{+} ions to the aqueous phase as shown in Fig. 5.12.
Fig. 5.11. IR spectrum of binary Eu\textsuperscript{3+}-H\textsubscript{2}SbBP complex.
In view of the better extraction efficiency observed, $H_2SbBP$ was chosen for further experimentation, especially to study the synergistic extraction in the presence of various mono and bifunctional organophosphorus extractants ($S$). To evaluate the synergistic effect, the extraction behaviour of $Ln^{3+}$ ions from 1.0 mol dm$^{-3}$ sodium nitrate solution of pH = 3.0 with mixtures of $H_2SbBP$ and $S$ was investigated. The extraction efficiency of $Ln^{3+}$ ion was found to be negligible with $S$ alone under the investigated conditions. However, with mixtures of $H_2SbBP$ and $S$, considerable synergistic enhancement in the extraction efficiency of $Ln^{3+}$ ions was observed (Table 5.1). Synergistic enhancement factor was
also found to increase with increasing concentration of S. It is clear from the plots (Figs. 5.13-5.15) of \( \log D_{\text{syn,m}} \) vs. \( \log [\text{H}_2\text{SbBP}] \) at constant S that two molecules of H\(_2\)SbBP are involved in the synergistic extracted complexes. Further, the extraction efficiency of Ln\(^{3+}\) ion increases linearly with increasing H\(_2\)SbBP concentration. The effect of concentrations of various S on the extraction efficiency of Ln\(^{3+}\) ion was also examined at constant H\(_2\)SbBP concentration (Figs. 5.16-5.18). The extraction efficiency of Ln\(^{3+}\) ion was found to increase linearly on increasing the concentration of S. From the log-log plots, it is clear that one molecule of S is involved in the synergistically extracted complexes. The effect of pH on the extraction behaviour of Ln\(^{3+}\) ions at constant H\(_2\)SbBP and S concentrations shows an inverse dependence on acidity and indicates the release of three H\(^+\) ions to the aqueous phase by reacting with three \( \beta \)-diketone donor sites of two molecules of H\(_2\)SbBP (Figs. 5.19-5.21).

![Graph](image)

**Fig. 5.13.** Effect of concentration of H\(_2\)SbBP on the extraction of Nd\(^{3+}\) ion at a: [S] = 0, b: [TBP] = 0.1 mol dm\(^{-3}\), c: [CMPO] = 0.005 mol dm\(^{-3}\), d: [TOPO] = 0.01 mol dm\(^{-3}\).
Fig. 5.14. Effect of concentration of H₂SbBP on the extraction of Eu³⁺ ion at a: [S] = 0, b: [TBP] = 0.1 mol dm⁻³, c: [CMPO] = 0.005 mol dm⁻³, d: [TOPO] = 0.01 mol dm⁻³.

Fig. 5.15. Effect of concentration of H₂SbBP on the extraction of Tm³⁺ ion at a: [S] = 0, b: [TBP] = 0.1 mol dm⁻³, c: [CMPO] = 0.005 mol dm⁻³, d: [TOPO] = 0.01 mol dm⁻³.
Fig. 5.16. Effect of concentration of S on the extraction of Nd\(^{3+}\) ion at constant \([\text{H}_2\text{SbBP}] = 0.005 \text{ mol dm}^{-3}\) for TOPO and 0.01 mol dm\(^{-3}\) for TBP and CMPO.

**Table 5.1.** Synergistic enhancement factors of \(\text{Ln}^{3+}\) ions with \(\text{H}_2\text{SbBP}\) in the presence of neutral organophosphorus extractants.

<table>
<thead>
<tr>
<th>S</th>
<th>([\text{H}_2\text{SbBP}])</th>
<th>([S])</th>
<th>(\text{Nd}^{3+})</th>
<th>(\text{Eu}^{3+})</th>
<th>(\text{Tm}^{3+})</th>
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<tr>
<td>TOPO</td>
<td>(5 \times 10^{-3})</td>
<td>(7 \times 10^{-3})</td>
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<td>16</td>
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<td>20</td>
</tr>
<tr>
<td></td>
<td>(1 \times 10^{-2})</td>
<td>(8 \times 10^{-3})</td>
<td>16</td>
<td>14</td>
<td>22</td>
</tr>
<tr>
<td></td>
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<td>20</td>
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<td>27</td>
</tr>
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</tr>
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<td></td>
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<td>(15 \times 10^{-2})</td>
<td>12</td>
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<td>26</td>
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Fig. 5.17. Effect of concentration of $S$ on the extraction of $\text{Eu}^{3+}$ ion at constant $[\text{H}_2\text{SbBP}] = 0.005 \text{ mol dm}^{-3}$ for TOPO and $0.01\text{ mol dm}^{-3}$ for TBP and CMPO.

Fig. 5.18. Effect of concentration of $S$ on the extraction of $\text{Tm}^{3+}$ ion at constant $[\text{H}_2\text{SbBP}] = 0.005 \text{ mol dm}^{-3}$ for TOPO and $0.01\text{ mol dm}^{-3}$ for TBP and CMPO.
Fig. 5.19. Effect of pH on the extraction of Nd$^{3+}$, Eu$^{3+}$ and Tm$^{3+}$ ions; 
$[\text{H}_2\text{SbBP}] = 0.005$ mol dm$^{-3}$ and $[\text{TOPO}] = 0.01$ mol dm$^{-3}$.

![Graph showing Log $D_{syn,m}$ vs pH for Nd$^{3+}$, Eu$^{3+}$, and Tm$^{3+}$](image)

Slope = 3.0 ± 0.1

Fig. 5.20. Effect of pH on the extraction of Nd$^{3+}$, Eu$^{3+}$ and Tm$^{3+}$ ions; 
$[\text{H}_2\text{SbBP}] = 0.01$ mol dm$^{-3}$ and $[\text{TBP}] = 0.1$ mol dm$^{-3}$.

![Graph showing Log $D_{syn,m}$ vs pH for Nd$^{3+}$, Eu$^{3+}$, and Tm$^{3+}$](image)

Slope = 3.0 ± 0.1
Based on the preceding results, the synergistic extraction equilibrium of Ln$^{3+}$ ion with H$_2$SbBP in the presence of TBP, CMPO or TOPO (S) may be expressed as:

$$\text{Ln}^{3+}_{\text{aq}} + 2 \text{H}_2\text{X}_{\text{org}} + m \text{ S}_{\text{org}} \xrightleftharpoons{K_{\text{syn},m}} \text{Ln}^{3+}(\text{HX})_{m}\text{S}_{\text{org}} + 3 \text{H}^+_{\text{aq}}$$

where $m = 0$ or 1. $K_{\text{syn},m}$ represents the synergistic equilibrium constant.

$$K_{\text{syn},m} = \frac{[\text{Ln}(\text{HX})_{m}\text{S}]_{\text{org}}}{[\text{Ln}^{3+}]_{\text{aq}}[\text{H}_2\text{X}]^2_{\text{org}}[\text{S}]^m_{\text{org}}}$$

Thus the distribution coefficient, $D_{\text{syn},m}$, from Eqs. (3) and (8) can be written as

$$D_{\text{syn},m} = \frac{[\text{H}_2\text{X}]^2_{\text{org}}(K_{\text{ex}} + K_{\text{syn},m}[\text{S}]^m_{\text{org}})}{[\text{H}^+]^3(1 + \beta_1[\text{NO}_3^{-}]) + \beta_2[\text{NO}_3^{-}]^2)}$$
The interactions between a β-diketone and a neutral oxo-donor in chloroform are in general, weaker when the diluent itself has strong interaction with the neutral oxo-donor [Sekine et al. 1983]. Hence, it is assumed to have negligible interaction between H2SbBP and S in chloroform.

The adduct formation reaction in the organic phase and the stability constant, \( K_s \), is given by

\[
\text{Ln}(X)(HX)_{\text{org}} + m S_{\text{org}} \rightleftharpoons \text{Ln}(X)(HX)_m S_{\text{org}}
\]

Equilibrium constant, \( K_s \),

\[
K_s = K_{\text{syn},m}/K_{\text{ex}}
\]

The equilibrium constants of synergistic complexes (\( K_{\text{syn},1} \)) of these metal ions were deduced by non-linear regression analysis and are given in Table 5.2. The \( K_{\text{syn},1} \) value increases with decreasing ionic radii of these metal ions, for all the systems studied here.

The stability constant, \( K_s \), for the organic phase synergistic reaction of Ln3+ ion–H2SbBP chelate with S has also been calculated according to Eq. (11) and are given in Table 5.3. The complexation strength of Ln3+ ions with various S follows the order: TOPO > CMPO > TBP, which is in accordance with their oxygen basicity values.

Fig. 5.22 shows the correlations of Log \( K_{\text{syn},1} \) values of Ln3+ ions and the oxygen basicity values of S in terms of their \( K_H \) values, where \( K_H \) is the equilibrium constant for the HNO3 uptake by S expressed as:

\[
H^+_{\text{aq}} + NO_3^-_{\text{aq}} + S_{\text{org}} \rightleftharpoons HNO_3 \cdot S_{\text{org}}, \text{of various S [Sahu et al. 2000]. The sharp decrease of Log } K_{\text{syn},1} \text{ value of Ln3+ ions from TOPO to TBP mostly reflects in the decrease of their } K_H \text{ values. On the other hand, in the case of CMPO the Log } K_{\text{syn},1} \text{ values are found to be almost equal to}
\]
that of TOPO even though their $K_H$ values are widely different. This may be due to the bidentate nature of CMPO in the complexation with Ln$^{3+}$ ions [Nakamura and Miyake 1994].

**Table 5.2.** Two phase equilibrium constants ($K_{syn,1}$) for organic phase synergistic reaction of Ln$^{3+}$-H$_2$SbBP with S in chloroform.

<table>
<thead>
<tr>
<th>Extraction system</th>
<th>Log synergistic constant (Log $K_{syn,1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nd$^{3+}$</td>
</tr>
<tr>
<td>H$_2$SbBP + TOPO</td>
<td>-2.90 ± 0.03</td>
</tr>
<tr>
<td>H$_2$SbBP + CMPO</td>
<td>-2.92 ± 0.02</td>
</tr>
<tr>
<td>H$_2$SbBP + TBP</td>
<td>-4.32 ± 0.02</td>
</tr>
</tbody>
</table>

**Table 5.3.** Organic phase synergistic stability constants of Ln$^{3+}$-H$_2$SbBP-S in chloroform.

<table>
<thead>
<tr>
<th>Extraction system</th>
<th>Log stability constant (Log $K_s$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nd$^{3+}$</td>
</tr>
<tr>
<td>H$_2$SbBP + TOPO</td>
<td>2.74 ± 0.03</td>
</tr>
<tr>
<td>H$_2$SbBP + CMPO</td>
<td>2.72 ± 0.03</td>
</tr>
<tr>
<td>H$_2$SbBP + TBP</td>
<td>1.32 ± 0.03</td>
</tr>
</tbody>
</table>
5.2.3. Correlation of $^{31}$P NMR chemical shifts of neutral organophosphorus extractants with the synergistic equilibrium constants

$^{31}$P NMR spectral data may help in studying the influence of neutral organophosphorus extractants in the synergistic extraction systems, as there exists a strong correlation between the electron donor density on oxygen of P=O group in neutral organophosphorus extractant molecule and the extraction efficiency [Ionova et al. 2001]. Fig. 5.23 shows that the Log $K_{\text{syn,1}}$ value of Eu$^{3+}$ ion increases linearly with increase in $\delta$ ($^{31}$P) NMR chemical shift of the neutral O-bearing organophosphorus extractant (TBP < CMPO < TOPO). However, CMPO was found to have deviated from linearity. It may be due to the bidentate nature of CMPO in the complex formation with Eu$^{3+}$ ion as is also evident from the IR spectral data (Fig. 5.24) of Eu$^{3+}$-H$_2$SbBP-CMPO complex, where both P=O (1266 cm$^{-1}$) and
\( \text{C}=\text{O} \) (1633 cm\(^{-1}\)) stretching frequencies of CMPO have been shifted to lower wave numbers (1211 \& 1622 cm\(^{-1}\), respectively), indicating the involvement of oxygen atoms of both carbonyl and phosphoryl groups in complexation.

![Graph](image)

**Fig. 5.23.** Variation of Log \( K_{syn,1} \) values of Eu\(^{3+}\) ion with \( \delta \) \(^{31}\text{P} \) NMR chemical shift values of neutral organophosphorus extractants. 1. TBP 2. CMPO 3. TOPO.

Thus, the donor ability of the phosphoryl oxygen, which is correlated with the \( \delta \) \(^{31}\text{P} \) NMR chemical shift (i.e., a high electron density on the oxygen atom induces a low electron density on the phosphorus atom and thus a high value of the \( \delta \) \(^{31}\text{P} \) NMR chemical shift) is the key parameter for the increase in the extraction efficiency of Ln\(^{3+}\) ion with \( \text{H}_2\text{SbBP} \) in the presence of neutral organophosphorus extractants.
Fig. 5.24. IR spectrum of ternary Eu$^{3+}$-H$_2$SbBP-CMPO complex (KBr).

In the extracted complexes of Eu$^{3+}$-H$_2$SbBP-TOPO and Eu$^{3+}$-H$_2$SbBP-TBP, the P=O stretching frequencies (1143 and 1277 cm$^{-1}$ of the free ligands) were shifted to lower wave numbers (1140, 1264 cm$^{-1}$, respectively in TOPO and TBP) indicating the involvement of phosphoryl oxygen in the complex formation. Further, in the synergistic extracted complexes, the carbonyl stretching frequency of H$_2$SbBP (1633 cm$^{-1}$) was also shifted to lower frequencies (1622, 1629 & 1622 cm$^{-1}$ in Eu$^{3+}$-H$_2$SbBP-CMPO, Eu$^{3+}$-H$_2$SbBP-TOPO and Eu$^{3+}$-H$_2$SbBP-TBP, respectively) indicating the involvement of carbonyl oxygen of H$_2$SbBP in
the complex formation with Eu$^{3+}$ ion (Figs. 5.24-5.26). The IR spectra of the Eu$^{3+}$ ternary complexes show a broad absorption in the region 3000-3500 cm$^{-1}$ indicating the presence of water molecules in the complexes.

Fig. 5.25. IR spectrum of ternary Eu$^{3+}$-H$_2$SbBP-TBP complex (KBr).
Table 5.4 gives the separation factors (S.F.) between these Ln\(^{3+}\) ions, defined as the ratio of the respective equilibrium constants in H\(_2\)SbBP + S and H\(_2\)SbBP systems. The addition of a neutral oxo-donor to the Ln\(^{3+}\)-chelate system significantly improves the selectivity among Eu\(^{3+}\)-Tm\(^{3+}\) and Tm\(^{3+}\)-Nd\(^{3+}\) pairs. On the other hand, a moderate increase in the S. F. value has been observed in the case of Eu\(^{3+}\)-Nd\(^{3+}\) pair. However, the separation factors observed in the present synergistic systems are found to be lower than EHEHPA (Eu/Nd = 3.94) system [Bautista 1995], which is widely used as an extractant in Rare Earth Industry. Thus, the present synergistic
systems may find potential applications for the extraction and separation of lanthanoids as a group from mineral resources.

Table 5.4. Separation factors between \( \text{Ln}^{3+} \) ions with \( \text{H}_2\text{SbBP} \) and \( \text{H}_2\text{SbBP} + \text{S} \) systems.

<table>
<thead>
<tr>
<th>Extraction system</th>
<th>Separation Factors (S.F.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eu / Nd</td>
</tr>
<tr>
<td>( \text{H}_2\text{SbBP} )</td>
<td>2.72</td>
</tr>
<tr>
<td>( \text{H}_2\text{SbBP} + \text{TOPO} )</td>
<td>3.49</td>
</tr>
<tr>
<td>( \text{H}_2\text{SbBP} + \text{CMPO} )</td>
<td>3.32</td>
</tr>
<tr>
<td>( \text{H}_2\text{SbBP} + \text{TBP} )</td>
<td>3.58</td>
</tr>
</tbody>
</table>