CHAPTER-VI

SOLVENT EXTRACTION BEHAVIOUR OF SOME LANTHANIDES AND EARLY ACTINIDES
6.1 Introduction

Solvent extraction methods are the most powerful separation technique to be used in analytical laboratories as well as in industries. This method is extensively used for the separation of uranium from its ore, plutonium from spent fuel and final purification of uranium [1]. Solvent extraction in chemistry received further impetus ever since it was used in the reprocessing of nuclear fuels. Tri-n-butyl phosphate (TBP) replaced earlier proposed extractants like methyl isobutyl ketone (or hexone) for the extraction of plutonium and uranium from irradiated nuclear fuels in view of its many favourable properties. The interest in the use of neutral organophosphorus extractants was further enhanced since Peppard [2] demonstrated the capability of TBP as an effective separating agent for the individual rare earth elements. Though different types of extractants like β-diketones, organophosphoric acids, oximes, dithizones, sulfoxides, phosphine oxides and amides are studied for their extraction and separation ability, reports involving the macrocyclic ligands like crown ethers, cryptands, etc. are of relatively recent origin.

The quantitative interpretation and understanding of extraction mechanism involves the computation of distribution equilibria and measurements of distribution ratio [3-9].
6.2 **Principles of solvent extraction**

Study of the liquid-liquid extraction process which involves distribution of a solute between two immiscible solvents, needs the determination of distribution ratio, $D$

$$D = \frac{\text{Total concentrations of metal ion in organic phase}}{\text{Total concentrations of metal ion in aqueous phase}}$$  \hspace{1cm} (1)

The extent of extraction is expressed in terms of percent extraction given by

$$\% \ E = \frac{100 \ D}{D + (V_{aq}/V_{org})}$$  \hspace{1cm} (2)

where $V_{aq}$ is the volume of the aqueous phase and $V_{org}$ is the volume of the organic phase.

If $V_{aq} = V_{org}$, then

$$\% \ E = \frac{100 \ D}{1+D}$$  \hspace{1cm} (3)

6.3 **Separation factor ($\Delta K$)**

Under identical experimental conditions two metal ions can be separated from each other if they possess different distribution ratios. The separation factor, $\Delta K$, signifies the effectiveness of partition and is expressed as:

$$\Delta K = \frac{D_1}{D_2}$$  \hspace{1cm} (4)

where $D_1$ and $D_2$ are the distribution ratios of the metal ions under identical condition. The high value of separation factor ensures separation in a single stage extraction.
6.4 **Classification of extraction systems**

Extraction systems are classified on the basis of nature of extracted species, solute-solvent interaction, mechanism of extraction etc., although this classification is by no means rigid. The important classes of extraction systems are solvating solvents, halometallic acids, organophosphorus acids, chelate extractants, coordinatively unsolvated salts and basic extractants. The extraction system from which extractants are used for extraction in this work are discussed below.

6.4.1 **Extraction by chelating agents**

Chelating agents coordinate to the metal ion to neutralise its charge as well as to satisfy the coordination number requirements, so that the species having greater solubility in the organic phase are formed. The metal chelate may be cationic, neutral or anionic depending upon the functional groups of the ligand.

A number of chelating extractant groups such as \( \beta \)-diketones, 8-hydroxy-quinoline, dithizones, tropolones, oximes, have been shown to be fairly good extracting agents under specified experimental conditions.

\( \beta \)-diketones are extensively used in radiochemical laboratories for various separation [10]. The properties of \( \beta \)-diketones are
influenced by the nature of substituents. A series of β-diketones having general formula $R_1\text{CO-CH}_2\text{-CO-R}_2$, is presented in Table 6.1.

Table 6.1: β-diketones with general formula $R_1\text{-CO-CH}_2\text{-CO-R}_2$

<table>
<thead>
<tr>
<th>β-diketones</th>
<th>Abbrev.</th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$pK_a^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furoyltrifluoroacetone</td>
<td>FTA</td>
<td></td>
<td>-CF$_3$</td>
<td>8.50</td>
</tr>
<tr>
<td>Thenoyltrifluoroacetone</td>
<td>TTA</td>
<td></td>
<td>-CF$_3$</td>
<td>9.10</td>
</tr>
<tr>
<td>Benzoyltrifluoroacetone</td>
<td>BTA</td>
<td></td>
<td>-CF$_3$</td>
<td>9.20</td>
</tr>
<tr>
<td>Thenoylacetone</td>
<td>TA</td>
<td></td>
<td>-CH$_3$</td>
<td>12.35</td>
</tr>
<tr>
<td>Acetyl acetone</td>
<td>AA</td>
<td>CH$_3$</td>
<td>-CH$_3$</td>
<td>12.70</td>
</tr>
<tr>
<td>Benzoylacetone</td>
<td>BA</td>
<td>C$_6$H$_5$</td>
<td>-CH$_3$</td>
<td>12.85</td>
</tr>
<tr>
<td>Dibenzoylmethane</td>
<td>DBzM</td>
<td></td>
<td></td>
<td>13.75</td>
</tr>
</tbody>
</table>

*pK$_a^*$ = -Ve logarithm of the acid dissociation constants of the β-diketones in 75 vol % dioxane [11].

Simple β-diketones are found to be quite promising to extract metal ion from weakly acid solutions which are incapable of extracting from strongly acidic solution. The extracting power of β-diketone increases, whereas selectivity becomes poorer. There is another class of β-diketone where one of the keto group is a part of the cyclic/heterocyclic moiety Table 6.2 are better extractants than the simple β-diketones.
<table>
<thead>
<tr>
<th>β-diketones</th>
<th>Structure</th>
<th>R</th>
<th>Abbrev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-trifluoroacetyl cyclopentanone</td>
<td><img src="image" alt="Structure" /></td>
<td>-CF&lt;sub&gt;3&lt;/sub&gt;</td>
<td>TACP</td>
</tr>
<tr>
<td>2-trifluoroacetyl cyclohexanone</td>
<td><img src="image" alt="Structure" /></td>
<td>-CF&lt;sub&gt;3&lt;/sub&gt;</td>
<td>TACH</td>
</tr>
<tr>
<td>1-phenyl-3-methyl-4-acetyl pyrazolone-5</td>
<td><img src="image" alt="Structure" /></td>
<td>-CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>PMAP</td>
</tr>
<tr>
<td>1-phenyl-3-methyl-4-benzoyl-5-pyrazolone</td>
<td><img src="image" alt="Structure" /></td>
<td>-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>PMBP</td>
</tr>
<tr>
<td>1-phenyl-3-methyl-4-(3,5-dinitro)benzoyl-5-pyrazolone</td>
<td><img src="image" alt="Structure" /></td>
<td>-3:5(NO&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;</td>
<td>DMPP</td>
</tr>
<tr>
<td>1-phenyl-3-methyl-4-trifluoroacetyl pyrazolone-5</td>
<td><img src="image" alt="Structure" /></td>
<td>-CF&lt;sub&gt;3&lt;/sub&gt;</td>
<td>PMTFP</td>
</tr>
<tr>
<td>3-phenyl-4-benzoyl-5-isoxazolone</td>
<td><img src="image" alt="Structure" /></td>
<td>-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>PBI</td>
</tr>
<tr>
<td>3-phenyl-4-acetyl-5-isoxazolone</td>
<td><img src="image" alt="Structure" /></td>
<td>-CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>PAI</td>
</tr>
</tbody>
</table>
6.4.2 Solvating solvents

These are neutral ligands and extract uncharged metal complex from organic solution. The solvation of metal complex occurs as a result of removal of water molecules from hydration sphere rendering it more hydrophobic thereby facilitating the extraction. Ketones, alcohols, esters, ethers etc. belong to this group of extractants. Polyethers and glycols are also used as extractants but they are not in much demand.

Organophosphorus extractants like tri-n-butyl phosphate (TBP), tri-n-octyl phosphine oxide (TOPO) and sulfoxides, etc. belong to this category of extractants. Multifunctional organophosphorus extractants, phosphine sulfides, amides, carbamoyl methyl phosphonate and phosphine oxides have recently been used as neutral extractants.

\[
\begin{align*}
\text{C}_8\text{H}_{17} & \quad \text{P} = 0 \\
\text{C}_8\text{H}_{17} & \quad \text{P} = 0 \\
\text{C}_8\text{H}_{17} & \quad \text{P} = 0 \\
\text{C}_4\text{H}_{9} & \quad \text{P} = 0 \\
\text{C}_4\text{H}_{9} & \quad \text{P} = 0 \\
\text{C}_4\text{H}_{9} & \quad \text{P} = 0
\end{align*}
\]

(TOPO)  
(TBP)

6.5 Synergism

The phenomenon in which two extractants taken together extract a metal ion species with a much higher efficiency as compared to the normal additive effect of these extractants (separately) is called 'Synergism'. The converse of this effect is known as antagonism. The extraordinary surge of interest
which has followed from the discovery by Cuninghame et al. [12] of a synergistic effect in the extraction of rare earths attest to the importance of this phenomenon. In 1954, these authors reported that the extraction of Pr(III) and Nd(III) by mixtures of HTTA and TBP in kerosene was significantly larger than expected from the distribution ratios measured with either extractant alone. This phenomenon was noticed as early as 1879 by Vogel [13] in the extraction of Co(II) thiocyanate by an equimolar mixture of ether and amyl alcohol. However, synergism acquired its name only in 1958 when a group of workers [14] from Oak Ridge National Laboratory investigated the extraction of U(VI) by combinations of organophosphorus extractants. Later, extensive work was carried out on the synergistic extraction of di, tri- and tetravalent metal ions with different combination of reagents by two pioneering workers in this field, namely Irving and Healy. The increasing interest in this field is evident from the large number of papers and various reviews published in different Journals [15-19].

Extraction of metal ion $M^+$ with a chelating extractant HA alone is expressed by

$$
M^{n+}_{aq} + nHA_{org} \underset{K_{ex}}{\overset{K_{ex}}{\rightleftharpoons}} MA_{n(org)} + nH^+_{aq}
$$

(5)

when the neutral chelate $MA_{n}$ has an excess of coordination sites which further reacts with a neutral ligand (S), forming adduct complexes ($MA_{n}S$) in the organic phase.

$$
MA_{n(org)} + mS_{org} \underset{K_{syn}}{\overset{K_{syn}}{\rightleftharpoons}} MA_{n}mS_{org}
$$

(6)
The overall reaction of synergic extraction by the use of mixed extractants can be written by combining eqns. (5) and (6)

\[ M_{aq}^{n+} + nHA_{org} + mS_{org} \xrightleftharpoons[\beta_n]{\text{org}} MA_n^{m+} mS_{org} + nH^+_{aq} \]  

(7)

The stability constant is given by

\[ \beta_n = \frac{K_{\text{syn}}}{K_{\text{ex}}} \]

**Measure of synergism**

The synergistic coefficient (S.C) as defined by Taube and Siekierski [20] may be described as:

\[ \text{S.C.} = \log \frac{D_{(1,2)}}{D_1 + D_2} \]

where \( D_1 \), \( D_2 \) and \( D_{1,2} \) are the distribution coefficients of a metal ion between an aqueous and organic phase with the two extractants taken separately and with mixture of the two extractants. When S.C. > 0, the extraction is synergistic. The cases where extraction is S.C < 0 involve an antagonistic effect.

Synergism is a special case of general extraction behaviour although it has retained its separate identity due to complexity of the extraction equilibria and its potentiality in enhancing or suppressing extraction [7]. Synergistic extraction has found its applications in mutual separation and isolation of metals, recovery of metals from complex materials, determination of stability of metal complexes, etc. The addition of Lewis base not only enhances the extraction of metal ion but also makes it
possible to extract even alkali and alkaline earth metals which are usually unextractable owing to the low stability of the chelate and the remaining water molecule in the chelate [21]. The quantitative extraction of transplutonium elements from relatively acidic media in the absence of salting out agents is at present the principal field of application of synergic extraction in the analytical chemistry of transplutonium elements.

6.6 **Extraction with macrocyclic ligands**

The macrocyclic chemistry is fast expanding and understanding the coordination and solvent extraction behaviour of the lanthanides and actinides with these ligands is emerging as a challenging area of research. Successful utilization of some of the macrocyclic ligands is for isotope separations [22], ion selective electrodes [23], magnetic resonance imaging [24], radiopharmaceuticals [25], fluoroimmunoassays [26], etc.

*In spite of the great promise it holds, the chemistry of actinides with macrocyclic ligands, is not well understood. In the area of actinide separation with macrocyclic ligands, few exciting observations have been made in areas related to fuel reprocessing [27] and separation of super heavy elements [28]. Some macrocyclic ligands are suggested as very strong uranophiles [29] for concentration of uranium from sea water and as actinide sequestering agents [30], underlines the growing interest in the nuclear chemistry.*
It was long known that the naturally occurring cyclic ionophores, like valinomycin, nonactin etc., have ion selective transport properties. Valinomycin with several oxygen donor sites, showed selectivity for K⁺ ion over Na⁺ by a factor as high as $10^4$ [31]. However, the discovery of a class of synthetic macrocyclic compounds popularly known as the 'Crown ether' with similar ion selective properties was a pioneering effort leading to the emergence of a new area of research [32-34].

Over the years, structural modifications based on stereochemistry, geometry and topology of the host compound were made use of to synthesize ionophores of improved complexing ability and selectivity, the latest being "SPHERANDS" [35,36] and "CALIXARENES" [37,38]. Some workers recently reported even the incorporation of macrocyclic side chains to the new class of carbon clusters called fullerenes [39].

6.7 **Size selective extraction**

The hydrophilic interior and hydrophobic exterior of the macrocyclic ligands make them ideal extractants as they can transport metal ions across non-aqueous barriers. The size-selective nature of these ligands is considered as an added advantage. The first report on the size selective extraction came from Frensdorff [40] who studied the extraction of alkali metal ions using crown ethers. McDowell [41-44] and Takeda [45] have found that in the extraction of complexes of alkali and alkaline
earth ions with crown ethers even the synergistic effect appeared to be size selective. In many cases the 'synergism' is maximum where the correspondence is best between the metal ion size and the ligand cavity radius.

In case of size selective extraction processes there are several factors operative these factors are: Partitioning of macrocyclic ligand between the aqueous and the organic phase symbolized as $P_L$ which is an important parameter deciding the extractability of the metal ion. Smaller $P_L$ values imply higher aqueous solubility of the ligand which in turn leads to better complexation, resulting in higher extraction. The partitioning of the complex, presence of counter anion and the role of organic diluent also influence to a greater extent the extractability as well as selectivity by the macrocyclic ligand. Lower dielectric constant of the diluent leads to lower ion-pair dissociation in the organic phase resulting in better extraction. On the other hand, high dielectric constant solvents have better extractive properties than low polar solvents like benzene, toluene, etc. [46] due to favourable solvation energy.

6.8 **Extraction of lanthanide ions using macrocyclic ligands:**

**A Review**

Encouraging reports on the size selective extraction of alkali/alkaline earth metal ions using crown ethers [47-51] led to the logical extension of these studies to the lanthanide
ions. However, contradictory reports are available in the literature on this area of research regarding the size selective nature of extraction.

Tsay et al. [52] have investigated the extraction behaviour of trivalent lanthanide ions using nitrobenzene solutions of 15-crown-5, dibenzo-18-crown-6 and 12-crown-4 from aqueous solutions containing picric acid. The high extractability of Tb compared to others was explained on the basis of size compatibility. Samy et al. [53] have studied the ion pair extraction of trivalent lanthanides using 18-crown-6 in 1,2 dichloro-ethane and trichloroacetate as the counter anion. The decrease in extraction with increasing atomic number was explained on the basis of size selective complexation and impressive separation factors were reported (Table 6.3) as compared to HDEHP extraction method [54]. Frazier and Wai et al. [55] have observed the largest separation factors for lanthanide ions reported to date using 18C6 and ethylenediamine tetraacetic acid (EDTA) combination. Similar trends were also observed by Hasegawa et al. [56]. On the other hand, Khalifa et al. [57] observed that the heavier lanthanides were better extracted with 15C5 than the lighter ones which was explained on the basis of size compatibility. The extraction data of lanthanide picrates by 15C5 and 18C6 were interpreted by Nakagawa et al. [58] on the basis of the hydration characteristics of the metal ion size correlation was ruled out. They had concluded that the hydrated metal ion radius is too big to 'fit' into the ligand cavity. Recent reports by
Table 6.3: Separation factors for \((\text{DLn}^1/\text{DLn}^2)\) Ln(III) ions concentration of \(18\text{C6} = 0.01 \text{ M}\); Lithium trichloroacetate concentration \(= 2.0 \text{ M}\). Diluent: 1,2-dichloroethane; Temp. 298 K.

<table>
<thead>
<tr>
<th>Ln(^1)/Ln(^2)</th>
<th>Separation factor</th>
<th>Ref [53]</th>
<th>Ref [54]</th>
<th>Ref [59]*</th>
</tr>
</thead>
<tbody>
<tr>
<td>La/Ce</td>
<td>5.38</td>
<td>6.1</td>
<td>0.95 (0.89)</td>
<td></td>
</tr>
<tr>
<td>Ce/Pr</td>
<td>2.75</td>
<td>1.35</td>
<td>1.32 (0.95)</td>
<td></td>
</tr>
<tr>
<td>Pr/Nd</td>
<td>4.90</td>
<td>1.42</td>
<td>1.45 (1.07)</td>
<td></td>
</tr>
<tr>
<td>Sm/Eu</td>
<td>2.60</td>
<td>4.18</td>
<td>1.12 (1.12)</td>
<td></td>
</tr>
<tr>
<td>La/Pr</td>
<td>14.8</td>
<td>10.2</td>
<td>1.26 (0.85)</td>
<td></td>
</tr>
<tr>
<td>La/Nd</td>
<td>72.4</td>
<td>15.1</td>
<td>1.82 (0.91)</td>
<td></td>
</tr>
<tr>
<td>La/Sm</td>
<td>591</td>
<td>140</td>
<td>3.02 (0.95)</td>
<td></td>
</tr>
<tr>
<td>La/Eu</td>
<td>(1.54 \times 10^3)</td>
<td>320</td>
<td>3.39 (1.07)</td>
<td></td>
</tr>
<tr>
<td>La/Tb</td>
<td>(7.76 \times 10^3)</td>
<td>(2.80 \times 10^3)</td>
<td>- (3.16)</td>
<td></td>
</tr>
<tr>
<td>La/Tm</td>
<td>(9.99 \times 10^3)</td>
<td>(1.84 \times 10^5)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>La/Lu</td>
<td>(1.20 \times 10^4)</td>
<td>(1.24 \times 10^6)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ce/Eu</td>
<td>-</td>
<td>-</td>
<td>2.59 **</td>
<td></td>
</tr>
<tr>
<td>Pm/Eu</td>
<td>-</td>
<td>-</td>
<td>2.71 **</td>
<td></td>
</tr>
<tr>
<td>Tm/Eu</td>
<td>-</td>
<td>-</td>
<td>2.67 **</td>
<td></td>
</tr>
</tbody>
</table>

*Separation for 1:1 complex of 18C6; values inside parenthesis are for 1:2 complex.

**Ref [65].
Inoue et al. [59,60] involved extraction with H2O, D2O and H2O-D2O mixture as the aqueous phase. On the basis of solvent isotope effect they have suggested the extraction of three water molecules into the organic phase in such cases. Deorkar et al. [61] have studied the separation of cerium(III) from transition elements with 15C5. Extraction of trivalent f-elements by 18C6 and 15C5 in the presence of different hydrophobic anions was studied by Proyaev et al. [62]. Aly et al. [63] have used 12C4 and 15C5 as neutral donors for the extraction of some trivalent lanthanides (Nd3+, Tm3+ and Yb3+) and actinides (Am3+ and Pu4+) with HTTA in chloroform. The extraction of Eu3+ and Tb3+ ions with 12C4, 15C5 and 18C6 was studied by Jeong et al. [64] in dichloromethane. Ensor et al. [65] have studied the extraction behaviour of trivalent lanthanides using dinonylnaphthalene sulphonic acid and a substituted crown ether namely, 4-tert-butyl-cyclohexyl-15-crown-5 and observed a synergistic effect on extraction. The crown compound produced measurable enhancement in extraction of the lighter lanthanides, while Tm(III) was relatively unaffected, which they explained on the basis of size selective extraction. Similar conclusions were drawn by Tang et al. [66], who had used a 16 membered crown ether containing the carboxylate group and observed that the distribution ratio values decrease with decreasing ionic radii. Most recently, remarkable increase of an extractability and selectivity were achieved by Kitatsuji and co-workers [67], in the synergistic ion-pair extraction of lanthanides with 18C6 or dicyclohexano-18-crown-6 (DC18C6) in the presence of thenoyltrifluoroacetone. The author explained the
enhancement in the extraction on the basis of size-fitting effect in the complex formation of the lighter lanthanide ions with crown ethers. Shehata et al. [68], have studied the extraction of Eu(III) and Gd(III) with thenoyltrifluoroacetone and crown ethers in nitrate medium. The result indicate that the enhanced extraction is due to the formation of species $\text{M(NO}_3\text{)}(\text{TTA})_2.\text{CE}$. The extraction of lanthanides(III) and actinides(III) with different $\beta$-diketone (HA) such as thenoyltrifluoroacetone (TTA), trifluoroacetone (TFA), benzoyl trifluoroacetone (BTA) and 2-naphthoyl trifluoroacetone (NFA) was investigated by Meguro et al. [69] in 1,2 dichloroethane. The reports indicate synergic enhancement is due to $\text{MA}_2(\text{CE})^+ \text{ or MA}_3(\text{CE})$ complex, [where CE is 18C6] depending upon the kind of HA. The separation factors (S.F) between Am(III) and Eu(III) was in the order: SF(NFA) < SF(BFA) < SF(TTA) < SF(TFA). Dukov and Genov [70-72] have used B15C5 as synergists in the extraction of trivalent lanthanides ($\text{Pr}^{3+}, \text{Gd}^{3+}$ and $\text{Yb}^{3+}$) with 1-phenyl-3-methyl-4-benzoyl pyrazolone-5 (HPMBP) or thenoyltrifluoroacetone (HTTA) in different diluents. The composition of the extracted species have been reported as $\text{M(PMBP)}_3\text{CE}$, when benzene or chloroform was used as the diluents and $\text{M(PMBP)}_3.2\text{CE}$, when carbon tetrachloride was used as diluent. Mathur and Khopkar [73] have reported synergistic extraction of Eu(III) with 1-phenyl-3-methyl-4-trifluoro-acetyl pyrazolone-5 (HPMTFP) with DC18C6 and B15C5 and reported formation of self adduct species $\text{Eu(PMTFP)}_3.\text{HPMTFP.DC18C6}$ and with B15C5 as $\text{Eu(PMTFP)}_3.\text{HPMTFP.n B15C5}$ (n = 1 or 2). Another report by Ensor and Reynolds [74] in the extraction of trivalent Eu, Ce,
Pm and Tm with didocynaphthalene sulfonic acid and crown ethers such as dibenzo-18-crown-6 (DB18C6), DC18C6 and dibenzo-24-crown-8 (DB24C8) suggests size of the crown cavity has little effect on the synergistic mechanism. Imura et al. [75] have studied the extraction of lanthanides(III) with 18C6 in presence of penta-decafluorooctanoate (PDF0) and trichloroacetate (TCA) into 1,2-dichloroethane. The predominant species were found to be MA₃(18C₅6) where A is PDF0 or TCA. The extraction of La(III), Gd(III) and Lu(III) with hexafluoroacetylacetone (HFA) and 18C6 in benzene, chloroform and nitrobenzene solvent were studied by Imura et al [76]. The species responsible for synergism were M(HFA)₃(18C6) in benzene and M(HFA)₃(18C6)A. Where 'A' stands for the counter anion such as perchlorate and picrate in chloroform and nitrobenzene. Mechanism of extraction of trivalent europium from perchlorate medium by chloroform mixtures of thenoyltrifluoroacetone and 18C6 was studied by Shehata et al. [77]. Recently Imura et al. [78] have reported the extraction of La(III) and Eu(III) trichloroacetate complexes extracted with 18C6. They established the species [La(TCA)₂(18C6)(H₂O)ₙ]TCA (n = 1 or 2) coordination number 10 for La(III) and [Eu(TCA)(18C6)(H₂O)ₙ]TCA₂ (n = 1, CN = 8) and (n = 2, CN = 9) for Eu(III).

On the basis of the above mentioned reports, it can be concluded that though a majority of the workers on lanthanide-crown ether extraction have explained their results based on size selective extraction, it is quite intriguing that a large hydrated ion gets into the relatively small ligand cavity. Therefore,
it requires a fresh look at the subject. One of the objectives of the present study is to study the exact nature of speciation in such extraction systems. Structural work carried out with compounds isolated from homogeneous medium does not substantiate the model of encapsulated lanthanide ion with crown compounds [79-82] for solvents like water, methanol, acetonitrile, etc.

6.9 Extraction of actinide ions using macrocyclic ligands

An early report by Yakshin [83] suggested higher extraction of actinide ions (UO$_2^{2+}$, PuO$_2^{2+}$, NpO$_2^{2+}$, Pu$^{4+}$ and Np$^{4+}$) into 1,2 dichloroethane by DC18C6 and DC24C8 compared to that with DB18C6 and DB24C8. Much later Shukla et al. [84] have observed similar trends for UO$_2^{2+}$ and Pu$^{4+}$ with benzonitrile as the organic diluent which could be explained on the basis of the proton affinity constants of the crown ethers [85,86].

Some reports are available [63, 86-92] where the macrocyclic ligands act as auxiliary ligand (as a neutral oxodonor), the inner coordination sphere being occupied by more strong chelating ligands like NO$_3^-$, TTA$^-$ etc. As a consequence, no size selectivity is expected in these systems even though some authors have explained their results based on this aspect.