1.1 Introduction

In analytical chemistry, solvent extraction has come to the forefront in recent years as a popular separation technique because of its elegance, simplicity, speed and applicability to both tracer and macro amounts of metal ions. The aspects of solvent extraction with its applicability are very well explained [1, 2].

In the past century the technique of solvent extraction has grown into many folds and has becomes most powerful unit of operation. Solvent extraction enjoys a favored position because of its ease, simplicity, speed of operation and wide scope. Solvent extraction is economically cheap as it does not require any sophisticated apparatus or instrumentation; a separating funnel does the entire job of separation. Solvent extraction separation technique is a convenient and useful method. Its applications are innumerable and extend to a wide range of industries such as chemical, metallurgical, nuclear, petrochemical, food, pharmaceutical as well as in waste management. It can be employed to concentrate and separate metal ions and to determine stoichiometries and stability’s of complexes extracted into an immiscible liquid phases. The importance of solvent extraction leads back to the rapid growth of Science and Technology. Solvent extraction permits very simple and clean separation of materials at both micro as well as macro concentrations, hence it is employed very widely in both fundamental research and technology.

Solvent extraction operation consists of following steps:

1. Intimate contacting of solvent with the aqueous phase containing solute so that the solute is transferred from aqueous phase to the organic phase.
2. Equilibration of two phases.
3. Separation of two immiscible phases.
4. Back extraction of solute from the organic phase to aqueous phase by the use of suitable strippants.

The proceedings of International Conference on Solvent Extraction [ISEC] [3-20] are very important sources of information on the various
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aspects of solvent extraction and provide valuable records of the latest developments and trends in diverse areas of the field. The various aspects of solvent extraction are very well covered in several monographs by Treybal (21), Morrison and Freiser [22], Alders [23], De [24], Starry [25], Marcus and Kertes [26], De, Khopkar and Chalmers [27], Hanson [28], Sekine and Hasegawa [29], Zolotov [30].

1.2 Histology of Crown Ethers

Crown ether is a generic name given to macrocyclic polyethers containing ethylene bridges separating electronegative oxygen atoms. The discovery of macrocyclic polyethers is interesting in recent developments of separation chemistry. They typically contain central electron rich hydrophilic cavity with diameter varying from 1.2-6.0 Å. The hydrophilic cavity is ringed with electronegative binding hetero atoms such as oxygen, nitrogen, sulphur etc., which in turn are surrounded by a collar of -CH₂ groups forming a framework which is flexible and exhibits hydrophobic behavior. The hydrophobic exteriors allow them to solubilize ionic substances into non-aqueous solutions and in membrane media. Such properties facilitate for their use as extractants and membrane carriers. Macrocyclicpolyethers form much more stable complexes than open chain analogues. Apparently, this “macrocyclic effect” is due to the fact that cation is being completely surrounded by a cyclic macrocycle. Thus, when the inorganic cation fits into the cavity of crown ether or sandwiched between two crown ether molecules it becomes a lipophilic species. This property of crown ethers, converting inorganic cation into lipophilic species can be utilized in extractive separation analysis.

Pure chance discovered the first crown ether [31]. C. J. Pedersen was working as an industrial chemist for Du Pont. A project was initiated in the fall of 1961 by him, to find new vanadium containing catalysts for the polymerization of olefins. Pedersen decided to study the effects of uni and multidentate phenolic ligands on the catalytic properties of vanadyl group,
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quinque-dentate ligand selected was bis-{2-(o-hydroxy-phenoxy)ethyl} ether ‘C’ and the synthesis was began according to the route outlined in Fig-1.5.1. During the synthesis of ligand from catechol a small quantity of byproduct in the form of silky crystals was obtained, which showed strange solubility behavior, which led to further spectroscopic studies and resulted in the discovery of the first crown ether which was named as Dibenzo-18-Crown-6. Since then large number of crown ethers were synthesized. The discovery of crown ethers led to an enormous advances in chemistry.

For many years the co-ordination chemistry of alkali metal ions was completely ignored by chemists. The synthesis, properties and various applications of crown ethers have appeared in several monographs and review articles [32-97] giving new ideas in the use of crown ethers in separation science. Indeed, there was strong doubt that such coordination chemistry could even exists since it was universally accepted that the alkali ions in solution were inert, i.e. they were highly resistant to solvolytic, redox, or complexation reactions. A new era in the coordination chemistry of alkali elements was inaugurated by the discovery of crown ethers by Pedersen in 1967. During the past few decades inventive scientists have found many applications of crown ethers which includes synthetic organic chemistry, membrane transport, chromoionophores, fluoroionophores, ion chromatography, isotope separation, ion selective electrodes, molecular recognition, phase transfer catalysis and extractive separation analysis.
1.3 Classification of Crown Ethers

The organic neutral ligands are classified into three groups:

a) Podands  
b) Coronands  
c) Cryptands.

a) **Podands**: These are the open chain compounds and are characterized by lacking ring and bridge structures.

b) **Coronands**: These are cyclic compounds. Coronands containing oxygen as donor atoms are called crown ethers, those containing oxygen and nitrogen as donor atoms are called as aza-crown ethers and others containing oxygen and
sulphur as donor atoms are called as thio-crown ethers. Various crown ethers are shown in Fig-1.3.1.

c) Cryptands: These are macropoly cyclic polyethers and are classified into bicyclic, tricyclic and tetracyclic.

1.4 Nomenclature of Crown Ethers

The IUPAC names for the crown ethers are very long and it was not easy to use such names in routine days. It was very difficult to use such lengthy names for repeated use. Therefore a system of adhoc name, based upon the number and kinds of hydrocarbon rings, the total number of atoms in the ring, the class name “crown” and the number of oxygen atoms in the polyether ring, was developed for the purpose of naming. e.g., 1,4,7,10,13,16-hexaoxa cyclo octadecane is designated as 18-Crown-6. Here number 18 indicates the total number of atoms in the polyether ring while the number 6 denotes the number of donor oxygen atoms in polyether ring. Additional substituents or sites of condensation like dibenzo or dicyclohexano are written first, e.g., Dibenzo-18-Crown-6, Dicyclohexano-18-crown-6. The various crown ethers with their structures are shown in figure 1.4
C. J. Pedersen [1967] synthesized crown ethers and awarded the Nobel Prize in Chemistry in 1987 without having a Ph. D.

Figure 1.4 structures various crown ethers
1.5 Synthesis of various Crown ethers

Synthesis of crown ethers are done by straight forward condensation method using vicinal diols such as catechol and divalent organic group containing \((-\text{CH}_2\text{-CH}_2\text{-O})_n\text{-CH}_2\text{-CH}_2\text{-}\) moiety as shown in Figure1.4.1. The saturated crown ethers are prepared from the corresponding aromatic ones by catalytic hydrogenation in 2-butanol at higher temperatures and pressures over ruthenium catalyst. Recovery of the product is done by column chromatography on alumina.

![Chemical structures](image)

**Figure 1.5 Synthesis of Crown Ethers**
1.6 Characteristics of Various Crown Ethers

Various crown ethers are characterized by their different properties such as colour, solubility, melting point and characteristic absorption peaks. Crown ethers with aromatic side rings are colorless crystalline compounds. The saturated crown ethers are colorless viscous liquids or solids of low melting point. They are very much more soluble in all solvents than their aromatic precursors.

Saturated crown ethers do not show any absorption above 220 nm, the aromatic crown ethers show absorption band near 270 nm (in methanol) which are characteristics for catechol and its ethers. Complexing with cation brings about distinctive changes in this band generally by appearance of a second peak at about 280 nm, with changed absorbance of the main band. The molar absorptivity of these compounds varies from 1.2 - 8.4 x 10^3 cm^-1 mole^-1. The infrared spectra of aromatic as well as aliphatic crown ether shows the presence of ether linkages by a strong broad band around 1230 cm^-1 for aromatic-O-aliphatic and a band at 1100 cm^-1 for aliphatic-O-aliphatic group.

For a given polyether ring the melting point rises with a number of benzo- groups. Crown ethers containing more than one benzo- groups are nearly insoluble in water and sparsely soluble in alcohols and many other common solvents at room temperature. They are readily soluble in methylene chloride, ethylene chloride, chloroform, nitrobenzene. The saturated crown ethers are colorless viscous liquids or solids of low melting point. They are very much more soluble in all solvents than their aromatic precursors.

1.7 Extraction equilibria involved in solvent extraction with crown ethers

It is worthwhile to consider the extraction equilibria with reference to crown ether as an extractant. The extraction equilibrium between an aqueous phase of metal ion M^{n+}, counter anion A^- and an organic phase of the crown ether L can be represented by

\[ M^{n+} + L_o + nA^- \rightleftharpoons (MLA_n)_o \]
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\[ K_{ex} = \frac{[MLA_n]_o}{[M^{n+}][L]_o[A^-]^n} \]

Where \( K_{ex} \) is the extraction equilibrium constant, the subscript ‘O’ refers to organic phase. The extraction equilibrium is considered to be consists of the following constituent equilibria.

The distribution of free crown ether between the organic and aqueous phase:

\[ L \rightleftharpoons L_o \]
\[ D_L = \frac{[L]_o}{[L]} \]

Where \( D_L \) is the distribution constant of crown ether. The complexation reaction of crown ether with metal ion in the aqueous phase is represented by

\[ M^{n+} + L \rightleftharpoons ML^{n+} \]
\[ K_{ML} = \frac{[ML^{n+}]}{[M^{n+}][L]} \]

Where \( K_{ML} \) is the complex formation constant.

The ion pair extraction of crown ether-metal ion complex with the counter anion in the aqueous phase is given by the equation

\[ ML^{n+} + A^- \rightleftharpoons (MLA_n)_O \]
\[ K_{ex'} = \frac{[MLA_n]_o}{[ML^{n+}][A^-]^n} \]

If a non polar solvent is used as an organic phase, the dissociation of an ion pair MLA\(_n\) in the organic phase will be negligible.

\[ K_{ex} = \frac{K_{ML} \cdot K_{ex'}}{[ML^{n+}][A^-]} \]

The overall distribution ratio of metal ion can be represented by:
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\[ D = \frac{[M]_O}{[M]} \]

Where \([M]_O\) and \([M]\) represent total metal concentration in organic phase and aqueous phase respectively. Since the ion pair formation in the aqueous phase is minimum due to high dielectric constant of water, we have

\[ D = \frac{[MLA_n]_O}{[M^{n+}] + [ML^{n+}]} \]

The \([MLA_n]_O\) can be obtained experimentally. If \([M^{n+}] >> [ML^{n+}]\) then

\[ D = K_{ex} \cdot [A^-]^n \cdot [L]_O \]

From the above equations it is evident that in solvent extraction of metals \((M^{n+})\), with crown ether \((L)\) in presence of a counter anion \((A^-)\), the value of \(D\) will be maximum if the \([A^-]\) in organic phase is large or \([L]\) in aqueous phase is large. Alternatively, the magnitude of \(D\) will be large if the value of \(K_{ex}\) is largest, which is possible by having large value of \((MLA_n)_O\) with minimum value for the concentration of uncomplexed metal ion or maximum value for the concentration of crown ether in the aqueous phase. Since \(K_{ex}\) is directly proportional to \(K_{ML}\) and \(K_{ex'}\) and inversely proportional to \(D_L\), it is imperative to have maximum value for \(K_{ML}\). This is possible by having maximum interaction of metal ion with crown ether in the aqueous phase. Further \(K_{ex'}\) can be largest provided if \([MLA_n]_O\) is highest. In order to get maximum value for \(D\) and consequently \(K_{ex'}\) the magnitude of \(D_L\) should be smallest, which is possible by having concentration of crown ether largest in the aqueous phase.

1.8 Factors influencing extraction by crown ethers

Complexes are usually made up of two or more species which are held together by a force, the binding forces involved are either a pole-pole, pole-dipole or dipole-dipole in nature. The interaction of cation and crown ether is primarily of ion-dipole Interaction type. The various factors which affect extraction with crown ethers include, Distribution of ligand in the aqueous
The distribution of crown ether between the aqueous and organic phase influences the extraction of metal ions. The small $D_L$ value gives large value for $K_{ex}$. If few cryptands are soluble in water then its salt complex is also soluble in water which in turn lowers the extractability of the complex.

b) Size of the cation

The cavity diameter of the crown ethers and the diameters of the various cations are shown in Table 1.8. The size of the cation and the cavity diameter of the crown ether are of great importance. If the size of the cation matches with the cavity diameter of the crown ether then the metal ion gets extracted [98]. Smaller cations are strongly solvated and more energy is required for desolvation. On the contrary, larger cations are unable to attract the ligand; on the whole, the selectivity of metal ions for crown ethers cannot always be ascertained on the basis of the size of the cation as well as on the cavity diameter of crown ether. Thus, 15-crown-5 shows maximum affinity for potassium in methanol even though the diameter of sodium ion is closer to the cavity diameter of 15-crown-5. Sometimes, the complex formation with relatively smaller ion in comparison with the cavity diameter of the crown ether, offers a large electrostatic stabilization energy e.g., extraction of gallium from hydrochloric acid medium with 18-crown-6 [99].
Table 1.8 Cation, Ionic and Crown Ether Cavity Diameter

<table>
<thead>
<tr>
<th>Cation</th>
<th>Ionic Diameter (Å)</th>
<th>Crown Ether</th>
<th>Cavity Diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>1.36</td>
<td>All 12-Crown-4</td>
<td>1.2-1.5</td>
</tr>
<tr>
<td>Na⁺</td>
<td>1.94</td>
<td>All 15-Crown-5</td>
<td>1.7-2.2</td>
</tr>
<tr>
<td>K⁺</td>
<td>2.66</td>
<td>All 18-Crown-6</td>
<td>2.6-3.2</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>2.94</td>
<td>All 21-Crown-7</td>
<td>3.4-4.3</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>3.34</td>
<td>All 24-Crown-8</td>
<td>4.5-5.0</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>1.98</td>
<td>All 30-Crown-10</td>
<td>&lt; 6.0</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>2.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>2.68</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>1.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo⁶⁺</td>
<td>1.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>U⁶⁺</td>
<td>1.66</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

c) Charge on the cation

Charge on the cation plays very important role on the extraction of metal ions by crown ethers. The cation selectivity’s of various ions with different charge, can be explained in terms of the difference in their $K_{ex}$ values. When the charge on the ion is large, invariably the size of the ion will be small, consequently complex formation will offer a large electrostatic stabilization energy. e.g., lithium will not form complex with 18-crown-6 because of small ionic size and low charge but gallium with small size and higher charge, forms strong complex with 18-crown-6 [99]. Similarly potassium ion (2.66 Å) and barium ion (2.68 Å) are almost identical in size but the selectivity with 18-crown-6 in methanol is more for barium than potassium. For smaller cations e.g., sodium (1.94 Å) and calcium (1.98 Å) which are similar in size, the selectivity for sodium ion is more than calcium ion. Thus for 18-crown-6, the cations which are larger in size and capable of fitting cavity of crown ether
have the selectivity scale divalent cation > monovalent cation, but for cations with smaller size the selectivity scale is reversed. This rule is not applicable everywhere, e.g. Tl⁺(2.94 Å°) and Rb⁺ (2.94 Å°), the $K_{ML}$ values with 18-crown-6 are 1.23 and 0.62 respectively [100].

d) Nature of donor atoms

The nature of the donor atom plays an important role in determining the selectivity of the complex, e.g., if the ligand contains sulfur atoms, it enhances the complexation, thus for silver, dithia-18-crown-6 is better extractant than 18-crown-6. The stability of Ag⁺-dithia-18-crown-6 is greater than Ag⁺-18-crown-6 complex. The large size of sulphur atom (1.85 Å°) increases the value of cation dipole distance and also the increased van der Waal’s repulsion between the sulphur atom and adjacent oxygen atoms result in the loss of complex stability [101-102]. If the nitrogen atom is substituted for oxygen atom in 18-crown-6, the stability of the resulting complex decreases because the van der Waal’s radius of nitrogen atom (1.5 Å°) is larger than that for oxygen atom (1.4 Å°) and the dipole moment of nitrogen donor atom group is smaller than that of oxygen donor atom group [103-104], with pyridine nitrogen the stability drops only slightly [105-106]. When ether oxygen in crown ether is replaced by ester oxygen groups, the stability of complexes decreases significantly.

e) Nature of diluents

Nature of diluents largely affects the extraction by crown ethers. In solvent extraction, the extractability and selectivity, with crown ethers are greatly affected by the organic solvents. The dielectric constant of the diluent as well as the solubility of crown ether in the organic phase is extremely important. Danesi et al. [107] investigated the extraction of alkali metal picrates by dibenzo-18-crown-6 into nitrobenzene- toluene mixtures, in which the dielectric constant varies from 3.4-35.0. The extraction equilibrium constant shows that the extractibility of alkali metal ions decreases, as the diluent composition is varied from pure nitrobenzene to pure toluene. Similar
results were obtained for the selective extraction of KCl with dibenzo-18-crown-6 and dicyclohexano-18-crown-6 [108-110]. This was explained in terms of extractibility from the viewpoint of anion solvation [111]. Rais et al. [112] extracted sodium and cesium dipicryl aminate by dibenzo-18-crown-6 into various solvents such as chloroform, nitrobenzene, methylene chloride, chlorobenzene, propylene carbonate and nitromethane. The distribution ratio for Na\(^+\) and Cs\(^+\) are the largest for chloroform where as for polypropylene carbonate and nitromethane it was smallest even though these two diluents are polar solvents. Iwachido et al. determined distribution ratio for potassium between aqueous potassium picrate and 57 organic solvents in presence of or absence of 18-crown-6. The presence of 18-crown-6 enhances the extractibility of potassium when the halogenated hydrocarbons were used but only slight enhancement was observed for oxygen containing solvents. Amongst the various diluents studied for the extraction of same element with crown ethers, methylene chloride was found to be the efficient solvent for the extractive separation analysis [113-115].

f) Nature of counter anion

In solvent extraction of metals with crown ethers, the nature of counter anion is very important. For the same crown ether-metal ion complex, the extractibility of ion pair into the same organic solvent is largely governed by the chemical nature of counter anion. In general the counter anion with large molar volume, such as picrate, dipicryl aminate, tetraphenyl borate and dinitrophenolate, makes the ion pair extraction more efficient. Other anions such as thiocyanate [116], iodide [117-119], bromide and perchlorate [120] have a degree of organophilicity which allow the metal ion extraction with crown ethers. Yakshin et al. [121] extracted dibenzo-18-crown-6-alkali metal ion complexes with various inorganic anions in to ethylene chloride. The extractibility sequence of anion was ClO\(_4^-\) > I\(^-\) > NO\(_3^-\) > Br\(^-\) > OH\(^-\) > Cl\(^-\) > F\(^-\). Crown ethers alone in low polarity solvents do not extract s- block elements or first row transition elements from dilute
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mineral acid solutions, this is because of large amount of energy required to remove the water of hydration from the anion or to transfer the hydrated anion to the organic phase [122]. In order to increase the distribution of metal complex with hard anion such as Cl\(^{-}\), NO\(_3\)\(^{-}\) and SO\(_4\)\(^{2-}\), carboxylic acid crown ethers were used [123-128], for which metal extraction does not involve concomitant transfer of the aqueous phase anion into the organic phase.

The extraction of 13 lanthanides with mixture of 8-hydro-quinoline (HQ) and crown ethers, dibenzo-18-crown-6 and dibenzo-24-crown-8 in dichloroethane from chloride medium were investigated [129]. A study on the highly efficient extraction of cesium ion by using calyx crown ether, bis(2-propyloxy)calyx[4] crown-6 was reported [130]. Novel pyrazolones, HPMP-A15C5 and HPMP-A18C6 were used for the extraction of divalent metal ions such as Mn\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\) and Pb\(^{2+}\) [131]. By using 18C6, DB18C6, DCH18C6 and DBP18C6 extraction and separation of La\(^{3+}\), Ce\(^{3+}\), Pr\(^{3+}\), Eu\(^{3+}\) and Er\(^{3+}\) cations in DMSO/water binary mixed solvent was carried out to inspect the influence of the trichloroacetic acid as counter ion on the stability and selectivity of the complexes formed between these cations and macrocyclic ligands [132]. Extraction ability and selectivity of tetra-aza-crown ethers for transition metal cations were studied [133]. The derivative of crown such as N-phenylbenzo-18-crown-6-hydroxamic acid was reported for the extraction and separation of thorium from monazite sand [134].

1.9 Scope and Methodology

Crown ethers have been used for the various studies pertaining to extraction equilibrium constant, stability constant and for spectrophotometric determination of some of the alkali and alkaline earth elements and other elements from p, d and f-block elements. No systematic efforts were made for the application of crown ethers in separation studies of various elements in
multicomponent mixtures. Crown ethers have been used extensively in the field of organic synthesis, for membrane transport studies, phase transfer catalysis, ion selective electrodes, molecular recognition, chromoionophores, fluoroionophores and for extractive separation analysis using chromatography and solvent extraction techniques. Therefore it was thought worthwhile to undertake systematic extraction and binary mixture separation studies of thorium(IV), uranium(VI), barium(II), strontium(II), beryllium(II), Lithium(I), sodium(I), potassium(I), Cesium(I), rubidium(I), cobalt(II), nickel(II), cadmium(II) and zinc(II) using crown ethers.
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