

A Review on Application of Crown Ethers in Separation of Rare Earths and Precious Metals



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Abstract Crown ethers are gaining importance in separation technology specifically for rare earth elements (REE, La to Lu plus Y) and precious metals (Au, Ag, Pt, Pd, Rh and Ir) due to their specific binding ability, metal complex stability and high extraction efficiency. The selectivity of crown ethers in extraction of these metals depends on different factors, including the cavity diameter and nature of a donor atom of the crown ether, size and charge of the metal ion, diluents and counter ion. Demand for strategic REE and precious metals are consistently increasing in the world while the separation of these metals is most challenging tasks. In this paper, the use of crown ethers in separation of REE and precious metals, reaction mechanisms and simplified process flowsheets will be elucidated. New reagents with high selectivity for the separation of these metals are further expected to produce high purity metals.

Keywords Crown-ether • Separation • Extraction • Rare-earths
Precious-metals

Introduction

The crown compound referred in this review may consist of a large cyclic (macrocyclic) compound having, as an electron-donating atom, a heteroatom such as an oxygen, nitrogen or sulfur in the ring structure and having a function to capture a cation in the hole of the ring structure. The crown compound may also include heterocyclic compounds having two or more heterocyclic rings. The characteristics and applications of the general class of crown compounds have been recognized for some time (e.g. [1–3]). Such macrocyclic compounds include molecules like cryptates, crown ethers, macrolides cyclic peptides, and Schiff bases.

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The special chemical and biological properties of these molecules have triggered significant interests in their synthesis, and investigations related to their structure and reactivity. Among several unique properties, they have a remarkable ability to encapsulate metal ions with high specificity and stability. In macrocyclic-metal ion complexes, a metal ion is placed at the center of cyclic environment of the ligand.

Macrocyclic polyethers were first reported in 1937, but it was not until 1967, when Pederson discovered [4] their abilities to bind alkali metal cations, that they drew significant attention. The impetus for molecular recognition in cation separation from aqueous solutions was given by Pederson, who reported on both the synthesis and metal ion complexation properties of several polyether macrocycles [5–7]. Crown ethers consist of repeating $(-O-CH_2-CH_2-)_n$ units. The basic crown ether is a molecule containing hydrogen, carbon and oxygen atoms. Each oxygen atom is bound between two carbon atoms and arranged in a ring, referred to as the “crown”. The term crown refers to the similarity of the molecular models of the compounds to a regal crown and to the ability of these compounds to crown cations by complexation. Pedersen’s original crown ether had six oxygen atoms exposed along the inside wall of the ring. Within about two decades from Peterson’s studies, the crown ether field developed into the field of guest-host chemistry [8] and then progressed to supramolecular chemistry [9, 10]. The achievements in these fields were recognized by the awarding of the 1987 Nobel prize in chemistry to *Charles Pedersen (DuPont)* [11], *Donald Cram (UCLA)* [12] and *Jean-Marie Lehn (France)* [13].

Pedersen [6] was the first to recognize that the compounds represent neutral synthetic molecules capable of forming stable complexes with metal ions including alkali, alkali earth, transition metal, and ammonium cations. He postulated that the cation in the complex is held in the center of the cyclic molecule of the crown ether by the electrostatic attraction between the positive charge of the cation and the negative dipolar charge on the oxygen atoms symmetrically arranged in the polyether ring. This postulation suggested that a relationship should exist between the size of the hole in the center of a crown ether molecule and the cation diameter. Data reported by Pedersen and Frensdorff [14] showed that the binding constants for metal ions are generally largest when the cation diameter is nearly equal to the hole-size in the cyclic molecule. Therefore, there are possibilities for certain cations to be selectively complexed by specific crown ethers.

The fundamentals of cation binding capacities can be found in treatises on this subject [15, 16]. An account of the future prospects for crown ethers has been examined in a book edited by Cooper [17]. During the past few years there has been increased activity in the field of macrocyclic compounds and their complexes. It has been recognized that many complexes containing synthetic macrocyclic ligands may serve as models for biologically important species. Crown ether macrocycles offer opportunities for molecular recognition studies (see [18]).

Crown Ether Type and Key Properties

The most common crown ether compounds are constructed with ethylene bridges separated by oxygen atoms ($-\text{CH}_2-\text{CH}_2-\text{O}-$) joined end to end to form the ring. The space inside the ring is of significance for applications involving these compounds. They are constructed using a modified Williamson Ether Synthesis to join individual monomers. These types of reactions can be adapted to create unique structures [19]. Substituted crown ethers can be used to provide the compounds with a wide range of properties.

The crown ethers are identified with a number representing the number of ring atoms, followed by a hyphen and the word "crown" and finally followed by another hyphen and a number referring to the number of ether linkages or oxygen atoms. For example, the chemical formula for 12-crown-4 may be $\text{C}_{12}\text{H}_{20}\text{O}_4$. An abbreviated form to denote crown ether compounds is 12C4 for 12-crown-4, DB18C6 for dibenzo-18-crown-6, and so on [20].

Several types of crown ethers have been synthesized and proof-of-principle tested for specific uses. Some examples include: crown aminoethers, crown polythioethers, lariat crown ethers, proton-ionizable crown ethers and chiral macrocycles of the same type. The electron pairs present in the ring heteroatoms provide the molecule with the ability to complex a wide range of cations in the empty cavity present in the ring [19]. The structural feature allows a number of complexes to be formed with cation species [21]. Several uses of crown ethers have been identified and advanced to actual applications. Examples include use in: (1) metal organic frameworks; (2) metal ion separations; (3) inorganic synthesis; (4) phase transfer catalysis; (5) as medium for radioisotope separation; (6) electron transfer reactions; (7) production of sensors; (8) ion transport in membranes; and (9) sodium level control in blood.

Some relatively simple structures of crown ethers are illustrated in Fig. 1.

Metal Cation Separation Applications

In hydrometallurgy for metal separation from ores or waste solutions, different primary processes are employed (e.g. [22]). These include, solvent extraction (aqueous-organic extraction) (SX), supported liquid membrane (SLM) and solid-liquid extraction techniques such as ion exchange with chelating resins, impregnated resins and impregnated resins combined with fluidized bed, and two-phase aqueous-aqueous extraction (cloud point (CP) extraction). One other class of process referred to as solid-phase extraction (SPE) involves macroligands immobilized on a solid phase. This has evolved to find many applications in separating metal ions [23]. One such SPE application is Molecular Recognition Technology (MRT) [24, 25]. The polymer inclusion membrane (PIM) is another

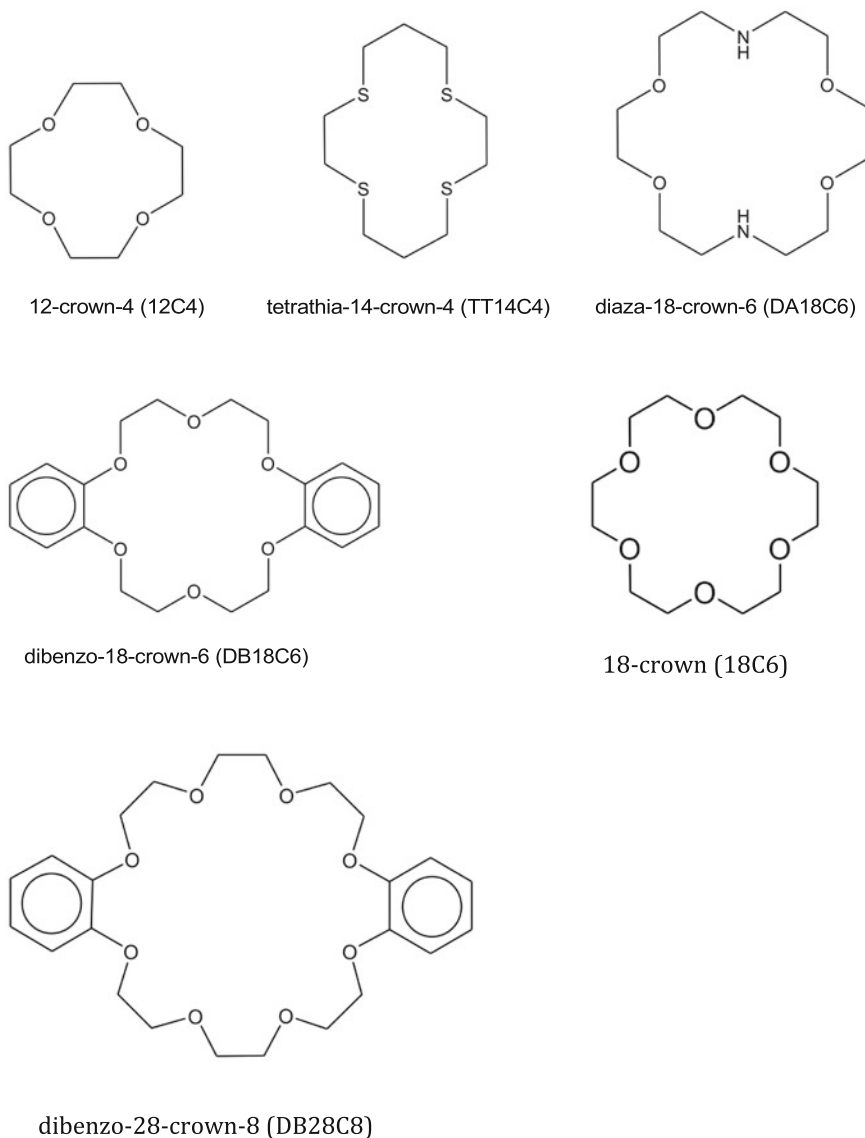


Fig. 1 Some crown ethers used for metal removal by solvent extraction

subset of the supported liquid membrane (SLM) process family. PIMs have the unique advantage of favorable system stability compared with SLM processes.

Organic solvent extraction has been the most favoured technology for metal separation and recovery in the past and now as a leading separation technology for metals [26]. The choice of organic extractants and aqueous solutions is influenced by several factors including technical performance, environmental impacts and cost

considerations. Organic ligands as metal extractants are exploited either alone or in mixtures in different media in diverse hydrometallurgical primary processes to achieve efficient separation of the desired metals. Among the processes, solvent extraction and solid-phase extraction have been increasingly employed for selective separation of metals. In this context, crown ethers and similar macroligands may play a key role as extractants either alone or in mixtures with other common organic extractant compounds or with compounds such as ionic liquids (e.g. [27]) to achieve synergistic separation of various metals. The action of macroligands causing interaction selectivity with metal ions results from their permanent dipole moment, polarizability and van der Waals radius (see for example, [28]). Data in the literature also suggest that the dipole moment and/or the polarizability decrease with the ligand radius and possibly increases the stability of the cation-ligand complex (e.g. [29]).

Cation Removal Mechanisms

Crown ethers have the ability to bind charged metal ions but also neutral molecules such as water, methanol, etc. through non-covalent interactions of van der Waals force and hydrogen bonding (e.g. [30]). The binding specificities have been described by similarities between cation size and crown ether cavity size. It seems that the relationship between cavity and cation size is a relatively simplistic view as several other parameters including interaction factors between the crown ethers, solvents, ions, add to the complexity.

When crown ethers undergo complexation with metal ions in a solvent extraction process they release protons, which enter the aqueous phase in exchange for the metal ion. This eliminates the need for concomitant transport of a counter anion into the organic phase. In practice the transfer of common counter ions such as Cl^- , NO_3^- and SO_4^{2-} , which are very hydrophilic, into the organic phase, is difficult and energy-consuming. In solvent extraction, the interaction between the cation and crown ether occurs mainly by ion-dipole effect. Factors affecting the interaction and thus extraction include: (1) crown ether structural cavity; (2) nature of donor atoms; (3) distributions of ligands in aqueous phase; (4) size of the cation; (5) charge on the cation; (6) nature of the diluent; and (7) nature of the counter ion.

The selectivity of the complex is determined also by the nature of the donor atoms [31]. The structural cavity size is proportional to the ring size and as a result crown ethers display selectivity in complexation based on cavity and ion size. There does not appear to be a simple correlation between cation size and ligand cavity diameter to predict favorable metal extraction. When the charge on the cation is large, the size of the metal ion will generally be small, resulting in large values for electrostatic stabilization energy (e.g. [32]). The dielectric constant of the diluent and the crown ether solubility in the organic phase are important for extractability and selectivity in solvent extraction.

The metal distribution ratio for the extraction process depends on both the thermodynamic driving force for cation complexation by a crown ether, and the solvation of the cation and counter anion by the organic solvent [33]. Conventional solvent extraction using crown ethers involves the transport of ion pairs from the aqueous phase to the organic phase. The formation of ion pairs helps to reduce the energy of transporting the ionic species into the organic phase, but the free energy gain is not sufficient to make up for the energy lost in solubilizing individual ions in the organic phase. This results in a low distribution ratio for the total extraction process.

The inability of organic solvents to solubilize ionic crown ether complexes and their counter ions is another obstacle in improving the separation efficiency in solvent extraction. The solvation free energies of simple counter anions such as the nitrates by organic solvents are unfavorable thermodynamically. A number of approaches were considered to solve this issue by the addition of hydrophobic anions to the aqueous solution, and the addition of hydrophilic solvents to the organic phase.

The solvation of crown ethers in room temperature ionic liquids has been considered more favorable thermodynamically than in the conventional solvent extraction system (e.g. [34, 35]). Here, the cationic crown ether complex and the counter anion are not expected to form ion pairs. Instead the individual ions are expected to be solvated separately by ionic species from the ionic liquids.

Synergistic extraction is defined as two extractants working together to extract a metal ion species with a much higher efficiency as compared to the normal additive effect of these extractants used separately (see [36, 37]). The cation transfer from an aqueous phase to an organic phase requires an extractant providing satisfactory solvation and coordination preferences for that cation (e.g. [36]). In many cases, one such extractant is sufficient but in some situations, more than one extractant is introduced, and these extractants work together cooperatively to yield effective cation transfer. The use of any two extractants in a synergistic extraction system provides two different objectives in the extraction process. The bulky extractant complexes with a metal cation and neutralizes charge while the second less bulky extractant is used to replace H₂O or occupy the open coordination sites.

Application of Crown Ethers in Separations Involving Rare Earth Elements and Precious Metals

Advances in the synthesis of selective extractants such as ionic and macrocyclic reagents including crown ethers have provided opportunities for the development of innovative approaches and applications in several areas involving separation of strategic metals within the rare earths and precious metals groups. Some relevant investigations on crown ethers alone or in combinations with other commonly used

extractants and/or ionic liquids for the separation and purification of rare earth and precious metals are discussed in the following section.

Rare Earth Elements and Separation with Crown Ethers

The rare earths are a homogenous group of metallic elements occupying the area consisting of 14 elements following lanthanum (La, 57), that is cerium (Ce, 58) through (Lu, 71) in group 3 of the periodic table. Yttrium (Y, 39) and scandium (Sc, 21) and lanthanum are also included with the rare earths because of their chemical similarities and common occurrence together in nature (e.g. [38]). The rare earth elements (REE) are divided into a heavy group (Tb through Lu), which are finding increased use as society evolves from a carbon-based to an electron-based economy, and a light group (La, and Ce through Gd), finding increased application in modern green technology.

The general method of recovering rare earth elements involves concentrating the ores using ore beneficiation techniques such as flotation, gravity or magnetic separation (see [22]). The concentrate is commonly leached with aqueous inorganic acids such as HCl, H₂SO₄, or HNO₃. After filtration or decantation and washing of the leach residue solids, the acidic liquor is treated by one or more methods based precipitation, solvent extraction, anion and cation exchange to produce either separated rare earth elements or a mixed rare-earth product. The choice of extraction reagents from among cation exchangers (based on carboxylic or phosphoric acid compounds), chelating exchangers (derivatives of β -diketones), solvating extractants (derivatives of phosphorous esters, phosphine oxides) and anion exchangers (based on primary and quaternary amines) have been extensively studied. Commonly used commercial extractants include di-2-ethylhexylphosphoric acid (D2EHPA), 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEHEHP), bis (2,2,4 trimethylpentyl) phosphinic acid (Cyanex[®] 272), C7 carboxylic acid (Versatic 10), tributyl phosphate (TBP) and C8-C10 quaternary amine (Aliquat[®] 336) (see e.g. [38]). To obtain the desired separation and purity of individual rare-earth elements from a mixed rare earth precipitate that has been purified of unwanted elements like U, Th, Fe and Al among others, hundreds of equilibrium stages of extraction equipment contacting organic and aqueous phases are employed.

Advances in the synthesis of macrocyclic ligands [8] including crown ethers have opened up new opportunities for use of these agents as selective and efficient extractants for separating and purifying rare earth elements. The crown ethers can be used as neutral oxodonors for the synergistic extraction of various metal ions with chelating, acidic or neutral extractants. One special group of reagents with phosphoryl groups in the acyclic part of the ligand has gained interest in the extraction of REE and to obtain varying extraction capacity and selectivity [39].

Furthermore, the additions of ionic liquids [35, 40] and synergistic extractants (e.g. β -diketones) to the extraction system [36] with crown ethers are expected to enhance extraction and separation performance of rare earth elements with simultaneous economic and environmental benefits.

In the published literature several laboratory-scale experimental results are reported for various rare-earth separations with crown ethers in combination with other extractants/additives looking at a number of variables to demonstrate metal complexation, separations performance and efficiency enhancements. The bulk of the studies have involved synthetic solutions of single or mixed rare earths in various media, in particular chloride medium. Only limited studies have reported separations using ore leachate solutions containing rare earths.

Crown Ethers as Extractants in Rare Earth Separation

Several studies have examined crown ethers to extract individual rare earths from aqueous solutions: Tsay et al. [41] using crown ethers, such as 15-crown-5, 12-crown-4 and dibenzo-18-crown-6, extracted individual rare earth ions from aqueous picrate solutions into nitrobenzene solution. They observed that Tb^{3+} , Eu^{3+} , Gd^{3+} , Nd^{3+} and Yb^{3+} can be easily extracted using 15-crown-5; however, the extraction of Ce^{4+} , Sm^{3+} , Dy^{3+} and Lu^{3+} was more difficult. Crown ethers of various sizes and substituents have been used in the extraction of REE [42, 43]. The crown ether, 18-crown-6 has been investigated for its effectiveness for rare-earth separation. For example, a quantitative separation of Ce^{4+} (3.57 mol/dm^3) by 18-crown-6 (0.07 mol/dm^3) from 4 mol/dm^3 HNO_3 solution containing other lanthanides into kerosene was achieved [44]. They found cerium extraction to depend on nitrate ion and extractant concentrations but not on pH and nitric acid concentration. The cerium extraction increased with the diluent's polarity. Several alkyl derivatives of 18-crown-6 have been used to separate rare earth elements and Am^{3+} from aqueous acidic solution [45]. Several crown ethers (15-crown-5, 12-crown-4 and dibenzo-18-crown-6) have also been employed [20] in the extraction of Tb^{3+} , Eu^{3+} , Gd^{3+} , Nd^{3+} , Yb^{3+} , Ce^{4+} , Sm^{3+} , Dy^{3+} and Lu^{3+} from aqueous solutions containing picrate into nitrobenzene solution.

The use of azacrown ether for extraction has also been studied [46–50]. Reagents such as 1,10-diaza-18-crown-6, 15-crown-5, benzo-15-crown-5, monoaza-, and tetraazacrown have been examined in extraction studies. Mono-aza dibenzo 18-crown-6 ether has been reported to extract La^{3+} , Nd^{3+} and Sm^{3+} efficiently in synthetic solutions in solid-phase extraction (ion exchange). The results gave a concentration factor (= ratio of lanthanide concentration in loaded eluate to that in initial feed solution) of 120 for La^{3+} , 131 for Nd^{3+} and 151 for Sm^{3+} [51]; also see [52]. A selective extraction of Y^{3+} over Sr^{2+} has been demonstrated by Wood et al. [53]. They showed that by changing the carboxylic acid at the terminal end of the lariat to hydroxamic acid, the Y^{3+} selectivity was greatly increased leaving a fraction having >99% Sr^{2+} .

Crown Ethers as Synergistic Extractants in Rare Earth Separation

Crown ethers have been added to synergistically enhance extraction [54, 55] of Ce^{3+} , Pm^{3+} , Eu^{3+} and Tm^{3+} with di-dodecyl-naphthalenesulfonic acid. Similarly, [56] observed synergistic effects in the extraction of Pr, Gd and Yb with benzo-15-crown-5 with heptanoic mixtures, but mixtures of heptanoic acid dicyclohexano-18-crown-6 and 18-crown-6 produced antagonistic effects. Improved extraction and separation of lanthanum and europium ions was observed for bis[2-ethyl-hexyl] phosphoric acid in the presence of 2-nitrobenzo-18-crown-6 [57].

Crown ethers have been used to extract La^{3+} , Ce^{3+} , Pr^{3+} , Eu^{3+} and Er^{3+} from acidic solutions in the presence of trichloroacetic acid (e.g. [20]). The presence of trichloroacetic acid to provide counter ions was shown to improve the selectivity of 18-crown-6 and its derivatives. Samy et al. [58] separated light rare earths from the heavy ones using 18-crown-6 and trichloroacetate. Imura et al. (1996) using a similar system (to that by Samy et al. [58]) to extract La^{3+} and Eu^{3+} as trichloroacetate complexes with 18-crown-6 in dichloroethane. They attributed selectivity of lanthanum relative to europium to the difference in the hydrations and structures of the complexes. For example, La was extracted as a monohydrate complex whereas Eu formed both mono-hydrate and di-hydrate complexes.

Separation efficiency improvements and selectivity of lanthanide and actinide extractions were found when crown ethers were used as neutral additives with chelating agents such as β -diketones, pyrazolones, and acid organophosphorous extractants [59, 60]. Demin et al. [61] reported that the extractability of 15 REE (except Sc and Pm) by di-tert-butyl-dicyclohexano-18-crown-6 (DTBDCH18C6) into an ionic liquid, 1,1,7-trihydrododecafluoroheptanol as the IL solvent phase (instead of the chlorohydrocarbons), yielded much higher extractability found with di-cyclohexano-18-crown-6 (DCH18C6) in 0.1 mol/dm³ HNO₃. Their results also showed that the addition of trichloroacetic acid or trifluoroacetic acid enhanced the metal distribution ratios and the difference in the separation factors of the elements were attributed to differences in stability constants of the extracted complexes.

A review by Petrova and Dakov [37] has referred to several synergistic extraction studies to separate members of the lanthanide series (e.g. [55, 62, 63]).

A study of the synergistic extraction of 13 lanthanides with 8-hydroxyquinoline (HQ) and 18-crown-6 or benzo-18-crown-6 in 1,2-dichloroethane by Atanassova [64] found that the addition of a crown ether increased the extraction efficiency, with 18C6 > B18C6. The overall equilibrium constant increased with increasing atomic number of the metal, and the difference between the equilibrium constant for extraction of a particular lanthanide with HQ-18C6 and HQ-B18C6 increased from La to Lu. It was also observed that the synergistic enhancement was the largest when 18-crown-6 was used in combination with 8-hydroxyquinoline.

Using a chelating extractant 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (HP) in the presence 18C6, B18C6 or DB18C6 crown ethers from aqueous chloride media (at 0.1 mol/dm³) and benzene as a diluent, Petrova and Dakov [37] examined the complexation of lanthanides (excepting Pm). Their results showed that the

addition of a crown ether to the chelating extractant, HP, increased the extraction efficiency with synergistic effects and gave a moderate increase in the separation factor between lanthanides. A selection of their results that illustrates these findings is given in Table 1. Data given in Table 1 for Synergistic Coefficient (SC) of an individual lanthanide and Separation Factor (SF) between two adjacent lanthanides in a mixture of two extractants are defined as follows:

$$\text{Synergistic Coefficient, } SC(\text{for lanthanide } M1) = \log\left\{\frac{(D_{E1,E2})_{M1}}{(D_{E1,M1} + D_{E2,M1})}\right\}$$

$$\text{Separation Factor, } SF(\text{for lanthanides } M1 \text{ and } M2) = \frac{(D_{E1,E2})_{M1}}{(D_{E1,E2})_{M2}}$$

where $(D_{E1,E2})_{M1}$ is distribution coefficient of a lanthanide M1 ion in the extractant mixture, E1 and E2, and $D_{E1,M1}$ & $D_{E2,M1}$ are distribution coefficients of lanthanide M1 in individual extractants, E1 and E2.

Crown Ether with Ionic Liquid as Diluent in Rare Earth Separation by Solvent Extraction

It has been reported [27] that for rare-earth metals in the presence of thorium, imidazolium based ionic liquids as diluents are more active than non-coordinating solvents such as kerosene. Ionic liquids based on quaternary ammonium and phosphonium with functional anions may be considered as bifunctional ionic-liquid extractants (Bif-ILEs) for REE extraction because of many desirable characteristics: (a) high extraction and selectivity; (b) low acid-base consumption; (c) easy stripping; (d) neutral complex extraction of Bif-ILE eliminates ammonia-nitrogen or high Na^+ , Ca^{2+} production in aqueous effluents, which is partly caused by extractants such as di-(2-ethylhexyl) orthophosphinate.

According to the observations by Liu et al. [27], Bif-ILE extractants show promise for high-value REE extraction. The use of these reagents has very attractive environmental benefits. Despite the potential advantages of applying ionic liquids either separately or in combination as bifunctional ionic liquid extractants, they have not been used for REE separation in industrial practice. These reagents will only become practical when the production cost for commercial quantities is reduced and the reagents have demonstrated their stability and ability to maintain high selectivity and loading capacity over many operating cycles.

Processes for Rare-Earth Extraction Based on Crown Ethers

(a) Cerium separation from monazite by solvent extraction

An extraction process using 18-crown-6 for cerium removal from Egyptian monazite has been described by El-Hefny et al. [44]. The monazite was ground to -200 mesh and digested with 50% NaOH solution at 140°C for 4 h. After dilution of the

Table 1 Synergistic coefficients (SCs) and separation factors (SFs) for extraction of lanthanides from aqueous chloride medium (pH = 3) using HP extractant with DB18C6 crown ether in benzene [37]

<i>Lanthanide</i>														
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
SC/HP-DB18C6	1.71	1.17	1.43	2.73	1.68	1.84	2.11	2.11	2.29	2.42	2.59	2.57	2.48	2.78
<i>Lanthanide pair</i>														
	Ce/La	Pr/Ce	Nd/Pr	Sm/Pr	Eu/Sm	Gd/Eu	Tb/Gd	Dy/Tb	Ho/Dy	Er/Ho	Tm/Er	Yb/Tm	Lu/Yb	
SF/HP	8.12	1.86	3.80	2.39	1.35	0.89	1.73	1.10	1.17	1.12	1.65	1.95	0.87	
SF/HP-DB18C6	2.39	3.31	1.52	10.71	1.94	1.65	1.74	1.65	1.58	1.65	1.58	1.58	1.73	

Note HP—4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one at 3.2×10^{-2} mol/dm³; DB18C6: dibenzo-18-crown-6 at 5×10^{-3} mol/dm³

mixture at 70–80 °C, the supernatant liquor was decanted and cooled. The hydrous oxide cake was washed. The assay for the cake was: 26.55% Ce, 13.00% La, 9.96% Nd, 2.96% Y, 1.65% Sm, 0.96% Gd and 5.26% Th. The hydrous oxide cake was dissolved in 4 mol/dm³ HNO₃ and held at 60 °C for 1 h while oxidizing Ce³⁺ to Ce⁴⁺ with sodium bromate to precipitate that element.

The nitrate solution containing lanthanide nitrate was subjected to solvent extraction by contacting and mixing with an organic solvent containing 0.05 mol/dm³ 18-crown-6 in kerosene at an organic to aqueous ratio of 2 at 25 °C for about 30 min. After phase separation, the organic phase was treated with 6 mol/dm³ HNO₃ to strip Ce and then the recovered Ce was precipitated as hydroxide by adding ammonia. The recovered Ce had a purity of 99% and the extraction and stripping efficiencies were 87% and 97%, respectively. It was found that the 18-crown-6 crown ether extraction for Ce was superior to the standard Aliquat 336 extractant in two key respects. A much higher concentration of 0.5 mol/dm³ Aliquat 336 was required to achieve similar results and an alcohol modifier that had to be added to eliminate third-phase formation when using Aliquat 336 was not required.

b Separation of REE from ore pregnant leach solution using macroligands-(Customized Superlig[®] Reagents) impregnated solids in a series of columns

IBC Advanced Technologies produces solid phase extractants (analogous to ion exchange resins) using active groups based on Molecular Recognition Technology (MRT) attached to solid substrates [24]. One of their trademarked solid-phase-impregnated macroligands, Superlig[®] (details on the chemical compound(s) are not available in the open literature) was applied to separation of sixteen REE from the pregnant leach solution produced by leaching ore provided by Ucore from the Bokan Dotson-Ridge REE deposit in southeast Alaska [65]. According to the report of work carried out by Hazen Research of Golden, Colorado, Ce and Sc were separated first using a customized Superlig[®] in a column configuration. The residual REE were then separated into light REE plus yttrium and heavy REE groups. Then selective separations of the individual REE in each group were achieved. The metals were eluted from the columns with small amounts of acid solution to obtain concentrated solutions of pure metals and it is reported that the purity achieved was >99% for each separated element. Finally, the individual metals were precipitated as carbonates.

Precious Metals Separation with Crown Ethers

Precious Group Metals (PGMs) are rare metallic elements of high economic value. Precious metals are chemically less reactive than most elements, have high luster, and have high melting points. The best-known precious metals are gold, silver, platinum and palladium. Others include ruthenium, rhodium, osmium and iridium.

The principal process step in the existing commercial processes (see [22, 66]) start from HCl/Cl₂ leach solution and are based on solvent extraction (Anglo American Platinum, Johnson Matthey, Vale (Acton), MRR and Inco) or ion exchange (Impala Platinum), or precipitation (Krastsvetmet and Lonmin). Here, gold, palladium and platinum are separated. After the principal process step, the subsequent process steps involve a combination of solvent extraction, distillation and precipitation to separate ruthenium, rhodium and iridium. The Lonrho process uses precipitation for silver and gold, solvent extraction for palladium, platinum, iridium and ruthenium, ion exchange for rhodium and finally distillation for osmium separation. A variety of organic extractants have been used in different processes for different metal removal steps. Some of the reagents are: methylisobutylketone, beta-hydroxyl oxime, n-octylamine, dibutyl carbinol, dihexyl sulphide, tributylphosphate, and secondary and tertiary amines. Generally, ammonium chloride is used as a precipitation agent. For specific flowsheets, diethylene triamine has been used for precipitating rhodium.

An early investigation [67] looked at the complexation ability and complexes of platinum metals with crown ethers containing tertiary phosphine-substituted benzo groups. Several crown ethers were tested like H18C6, D16C4, bis-(benzothia-crownether) and cyclotetraethioether for silver complexation and separation by liquid membrane-separation (see [68]). Palladium complexation with DC18C6 and DDB18C6 crown ethers, and separation under solvent extraction conditions in chloride media has been reported [69]. Some efforts have been made to use crown ethers as solvent extraction reagents in the extraction of precious metals [70, 71] with additional counter anions added. Generally, the problems associated with the increased solubility of extractants in the aqueous phase are circumvented by the addition of counter anions to increase effective extraction. However, this can cause the negative effect of making metal-ion stripping more difficult, which limits on application of crown ethers. Some separation examples involving PGMs are summarized in the following sections.

Pd(II)-Pt(IV) Separation with Multidentate Crown-Ether Embedded Polyfunctional Biomaterial

Dhakal et al. [72], synthesized a crown ether with an incorporated lipophilic chitosan derivative in chloroform as diluent and tested its effectiveness in the extraction of synthetic solutions of Pd²⁺ and Pt⁴⁺ from HCl-based aqueous solution. The rationale for the selection of chitosan is that it is a polyfunctional and highly reactive polymer and its amino functional moiety is considered to be efficient for precious metal-ion uptake by ion-pair formation. Firstly, they converted chitosan to dialkylated chitosan using dimethyl anionic solution (NaH dissolved in dimethylsulfoxide) and bromodecane. In a separate reaction the dibenzo-18-crown-6 ether was converted into a carbonyl derivative through Duff reaction prior to incorporating into dialkylated chitosan by Schiff base formation. The product generated, diformylated dibenzo-18-crown-6 ether, was condensed with the lipophilic chitosan

to prepare the extractant multidentate crown-ether embedded polyfunctional bio-material. The extraction test results showed that at lower HCl concentrations, high extraction of Pd^{2+} and Pt^{4+} was achieved. Extraction declined as HCl concentration was increased due to competition of both metal cations for H^+ . There was increased selectivity for Pd^{2+} over Pt^{4+} attributed to a possible sandwiched configuration between the bi-functional ligands. Generally, the uptake kinetics for the cations was found to be very slow (e.g. 2 h) unlike conventional extraction.

Synergistic Extraction of Pt and Rh with Alamine 304 and Crown Ethers

Simple and synergistic extraction aspects were examined by Jyothi and Lee [28] to determine enhanced selectivity of separation between Pt and Rh in HCl solutions (0.1–7.0 mol/ dm^3) employing several crown ethers (CEs) (18-crown-6, benzo-15-crown-5, di-benzo-18 crown-6, and di-cyclohexane-18-crown-6) at a fixed concentration of 0.005 mol/ dm^3 , and conventional amine extractants (Alamine 304 and Alamine 336). The results showed that use of CEs alone gave only some separation between Pt and Rh but enhanced synergistic separations were obtained for mixtures of CEs and Alamine extractants. For example, the highest SF of 133 for Pt/Rh was obtained with 18-crown-6 + Alamine 304 in 5 mol/ dm^3 HCl solution as compared with 40 SF for Pt/Rh using only 18-crown-6. For all cases tested, as a synergistic extractant, Alamine 304 was found to be superior to Alamine 336 for Pt-Rh separation.

Solid-Phase Extraction of PGMs from Secondary Sources

Secondary sources may involve waste products such as spent catalysts, which are leached to recover their platinum group metal content. Here, the selective removal of the PGMs using molecular recognition technology (MRT) has been applied for Pt, Pd and Rh separations [73]; see also Bernardis et al. [74]. In this application, Pd, Pt, Rh and base metals in an HCl leach liquor were separated using a solid-phase extraction method involving customized Superlig[®] reagents containing a series of media. The media consist of cation and anion selective ligands that are covalently bonded to solid supports and loaded into ion-exchange type columns. Use of a series of different Superlig[®] media separated Pd, Pt and Rh in consecutive steps. The mechanism of separation for the Superlig[®] includes ligand exchange (Pd extraction) or ion-exchange ($[\text{PtCl}_6]^{2-}$). It should be noted this process route also incorporates scrubbing and stripping stages, similar to solvent extraction, with impurity scrubbing off the loaded solid-phase extraction media. Izatt [75] made a case for the superior performance of the MRT extractants over SX in waste recycle applications. Typically, single pass metal recoveries are >99% compared to lower levels with SX, in particular, when the PGM concentrations are low in the feed solution (a few mg/L). It was also suggested that despite the relatively higher cost of

Superlig[®] reagents, regeneration of the degraded solid-phase extraction media reduces the overall reagent cost. A commercial MRT based system is in use for Rh recovery from waste feed at the Tarnka Kikinzokia Kogyo K. K. operation in Japan [76].

Summary—Status and Outlook

- Several crown ethers including functional group (and cross-linking group)-substituted crown ethers have been identified for applications involving alkali and alkaline earth ion extraction generally and more specifically for rare earths (lanthanides) and to limited extent actinides. In the design and synthesis of macrocyclic ligands, it has been reported that it is easier to synthesize a compound with a definite structure than with a certain required property [77].
- Interests in using macrocyclic extractants for metal extraction have increased, mainly to improve selectivity and extraction efficiency. Other incentives for the adoption of these extractants include eliminating the use of organic diluents and volatile organics, and the formation of third-phases prevalent with non-cyclic reagents.
- Laboratory-scale synthesis of these compounds has been achieved, although commercial-scale production is limited.
- The fundamental aspects of cation binding and separation of several metal ions have been achieved for separations in chemical analysis.
- The first application for cation separation was made in the early 1990s [78] and is of special significance because the new solvent extraction process was based on a crown ether extractant, di-*t*-butylcyclohexano-18-crown-6 in nitrate aqueous solution and 1-octanol solvent. This was used to recover >99.7% Sr-90 in three extraction stages from a complex high-level radioactive solution containing several lanthanides.
- Although application of various crown ethers has been tested for selective and near-quantitative removal of various metals in the REE and PGM families, wider-scale commercial-scale applications are yet to be realized.
- The use of selective and efficient extractants including crown ether derivatives for separation and refining of precious metals is expected to increase. The introduction of such reagents in existing solvent extraction circuits, either alone or as additives to the existing extractant should be feasible.
- Ionic liquids appear to exhibit favourable opportunities either as an alternative to existing organic diluents or as extractants. According to the observations by Liu et al. [27], mixtures of bifunctional extractants and ionic liquids show promise for high-value REE extraction. The exploitation of crown ethers with ionic liquids in solvent extraction of value-added, high purity strategic metals in the REE and PGM groups is anticipated to provide opportunities for meeting favorable economic and environmental targets in the future.

- Macroligand-impregnated solid matrices used in the solid-phase extraction mode under the banner of molecular recognition technology are being used in applications related to selective and cost-effective separation of REE [24] and PGM [73, 76] from actual ore and ore-leach solutions, respectively.
- Several crown ethers can be procured from different countries. Companies in China (e.g. Jiangxi Native Produce Imp. and Exp., Shanghai Ruizheng Chem, Tech. Co., Ltd., Hangzhou Pharma and Chem Co., Ltd., Trust & We Group) can supply kilogram to tonnage quantities several crown ethers such as 15-crown-5, 18-crown-6, benzo 15-crown-5, dibenzo 16-crown-6, 12-crown-4, 4'-aminobenzo-15-crown-5 ether and 2-(allyloxymethyl)-18-crown-6 ether. Companies in Europe (e.g. TCI Europe N.V., Chemos GmbH, Werner-von-Siemens—Germany, Merck Schuchardt, Germany) can supply varying quantities of crown ethers such as 4,13-diaza-18-crown-6 ether and 18-crown-6. An Indian company Sri Hari Labs, Tiruvallur, supplies the three base crown ethers, 18-crown-6, 15-crown-5 and dibenzo-18-crown-6. The price of crown ethers varies widely (in the range of US\$ 100 to 600/kg) depending on the type and quantity of crown ether being procured. As with any specialty chemical, most crown ethers are generally manufactured and supplied upon procurement order. From the list of crown ethers available commercially, it appears the high price of these compounds reflects a relatively low current demand for the reagents.
- Parallel developments to improve reagent costs need to be pursued.
- Industrial-scale exploitation of crown ethers has been slow despite their ability to yield efficient and selective separation of a range of rare-earth elements and some precious metals.
- With regard to precious metals, again most extraction circuits continue to be based on conventional solvent extraction, ion exchange, and precipitation steps. The cost-benefits related to crown ether applications in precious metal separations are still not favorable.
- There are opportunities to produce and utilize stable, non-toxic and affordable extractants (e.g. crown ethers and/or synergistic crown ether-conventional extractants), and diluents (e.g. ionic liquids) with high extraction efficiency and selectivity for rare earths and precious metals in order to develop improved process flowsheets.

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