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Review

Review on extraction and separation of valuable metal ions from aqueous solution by crown ether

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ABSTRACT

In recent years, with the rapid development of the economy and society, pollution of valuable metal ions in wastewater has become a major challenge to environmental sustainability. In order to solve the pollution caused by metal ions, researchers have conducted continuous researches and explored various remediation methods. Crown ether has attracted great attention because of its ionic radius and cavity size matching well with metal ions, which makes it have the ability to selectively complex metal ions. This unique property enables the directed removal and recovery of metal ions and makes crown ethers increasingly popular in extraction and separation processes. In this paper, the research progress of crown ethers in the extraction and separation of valuable metal ions was reviewed, with emphasis on the principles, extraction systems and the key factors affecting the extraction process. This study can provide some technical support for the application of separation and extraction of valuable metal ions by crown ether.

1. Introduction

Metal ions are the main pollutants in the wastewater, posing significant and persistent threats to the environment and public health due to their toxic and non-degradable nature [1]. Therefore, the researches on wastewater treatment containing metal ions have been widely concerned by researchers from various countries [2–5]. At present, the separation methods for metal ions from wastewater mainly include adsorption [6–9], membrane separation [10,11], ion exchange [12,13], chemical precipitation [14,15], electrochemistry and extraction [16,17]. The adsorption and ion exchange methods are mainly used to separate and recover valuable metal ions from wastewater [18]. These methods have broad range of applications and can selectively separate specific metal ions with high preferentiality. However, the immobilization of absorbent and resin has always been a problem in the industry, and the reuse of absorbent and resin are also a problem, which has restricted the industrial application. The other methods to remove metal ions from wastewater also have many disadvantages, such as low recovery rate, long separation time, high cost, difficult maintenance of equipment, poor treatment effect and easy production of secondary pollution [19].

The extraction method is widely used in the separation and recovery of valuable metal ions in aqueous solution because of its convenience, great separation effect, simple operation and wide applicability [20,21]. Extractants play important role in the extraction process. Traditional extractants for separating valuable metal ions mainly include phosphorus-containing 2-ethylhexyl phosphate mono 2-ethylhexyl ester (P507), di-(2-ethylhexyl) phosphoric acid (P204) [22–24] and nitrogen-containing trialkylamine (N235), copper ion extractant (N902) [25,26], but all of them have certain limitations. In particularly, it is difficult to obtain high-grade metal products after recovery because of low selectivity. As scientific and technological advancements progress, conventional extractants have become inadequate for the efficient extraction and separation of valuable metal ions. Therefore, there is an urgent need to develop new extractants with improved efficiency and selectivity.

Crown ether (CE) is a kind of macrocyclic polyether with multiple oxygen–methylene structural units in its molecule. Its structure resembles a crown, so it was called CE. CE has simple structure and is very similar to natural ionic carriers in performance. In 1967, Pedersen [27] first discovered that crown ethers (CEs) have special complexing abilities for certain metal ions, which attracted people's attention. In 1971, Frensdorff [28] was the first one to extract sodium and potassium ions from sodium and potassium picrate solutions using two isomers of benzo-18-crown-6 (B18C6). After 1975, Japanese scholars successively

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published the achievement on the extraction equilibrium of alkali metals using CE [29–31], and explored the effects of anions and solvents on the extraction equilibrium [32]. In recent years, China has gradually developed a strong interest in CE in the fields of rare earths and lithium separation [33–35]. With the gradual deepening of scientific researches, CE has become an important extractant for the extraction and separation of metal ions, and also developed into a unique discipline "crown ether chemistry" [36,37].

The negatively charged oxygen atom on the CE ring can form stable complexes with metal ions through electrostatic interactions. Fig. 1 presents the associative diagram between CE and metal cations [38]. When the pore size of the CE is close to the diameter of cation, the formed complexes exhibit optimal stability [39–41]. In order to further improve the extraction and separation ability of CE, the spatial structure and pore size of the CE can be adjusted by regulating the type and quantity of donor atom, the size of CE ring, and the type of substituent. These adjustments of CE improve the selectivity for specific metal ions [42–45]. The rigid benzene rings can be introduced to enhance the structural strength of flexible CE rings and improve their stability after binding with metal ions [46–48]. In addition, the side chains modified by electron-withdrawing groups can be introduced into the CE ring to form stable complexes with metal ions [49].

In this paper, the extraction principles of metal ions by CE, the extraction system, include single extraction system and synergistic extraction system, the influencing factors of metal ions in the extraction process also systematically reviewed. And the future development direction of metal ion extraction by CE is also prospected.

2. CE Extraction System

CE, as an excellent extractant, is usually dissolved in organic solvents such as ethanol, benzene, chloroform, ordichloromethane to prepare organic phase. The organic phase is then mixed with water solutions to achieve separation and recovery of metal ions. In order to further improve the separation performance of valuable metal ions in aqueous solutions, researchers often introduce co-extractants. Therefore, the extraction system can be divided into single extraction system and synergistic extraction system.

2.1. Single extraction system

In the process of extracting and separating valuable metal ions, the commonly used CE include 18-crown-6 (18C6), 15-crown-5 (15C5), 12-crown-4 (12C4) and so on. CEs can be modified by grafting side chain groups to enhance their extraction and separation performance. Organic systems that use a single CE as an extractant, or single functionalized CE as an extractant, are all called "single extraction systems".

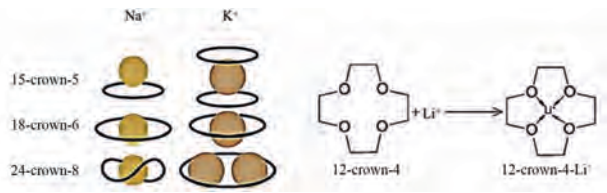

Fig. 1. Associative diagrams between CEs and metal cations [38].

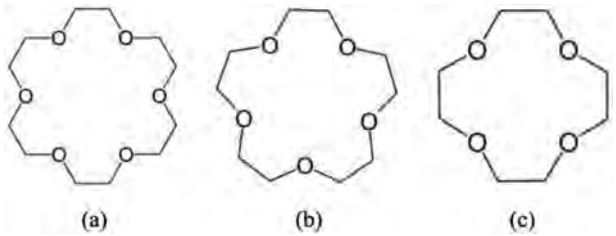

Fig. 2. Structure diagrams of CEs: (a) 18-crown-6, (b) 15-crown-5, (c) 12-crown-4.

2.1.1. 18-Crown-6

18-Crown-6 is a macrocyclic CE composed of 18 atoms in its cyclic structure, including 6 oxygen atoms and 12 carbon atoms (as illustrated in Fig. 2(a)). At the International Solvent Extraction Conference held in Lyon, France, it was first announced that it can be used as an extractant, in 1974 [50]. In this meeting, the research progress of extraction of Na^+, Cs^+, Ca^{2+}, Sr^{2+} and Ba^{2+} with dibenzo-18-crown-6 ether was introduced. The formation of complexes between CE and metal ions after extraction was studied, and the extraction equilibrium of alkaline earth and alkali metal by CEs was determined. The selectivity of CE in metal ion extraction was also discussed. Since then, CE have been widely employed as extractant for metal ion separation. Jing *et al.* [51] investigated the recognition mechanism of 18-crown-6 for various ions (K^+, Na^+, Li^+, Mg^{2+}, Fe^{3+}) in the single-ion and coexisting ions systems (K^+/Na^+ and K^+/Mg^{2+}) through molecular dynamics simulations. The results show that the selectivity order of 18-crown-6 for alkali metal ions in the solution phase follows $Li^+ \ll Na^+ > K^+ > Rb^+ > Cs^+$, the solvent environment has an important effect on the selectivity of 18-crown-6 for alkali metal ions.

Due to the presence of ether bonds, CEs have been shown to be efficient ligands for coordination of light rare earths, and 18-crown-6 ethers can coordinate with rare-earth elements (REEs) (III). However, because heavy REEs (III) with smaller ionic radii didn't match the cavity size of 18-crown-6 ether, it is difficult for 18-crown-6 ether to separate heavy REEs (III). Rodriguez-Blas group synthesized macrodipa by 1,3-diaza-18-crown-6 ether linked with two pyridinium carboxylic acids [52]. The studies on coordination with lanthanide elements found that the stability constant first decreased and then increased as the ionic radius of Ln(III) increased.

CE is an amphiphilic compound with certain water solubility. Once it enters the water phase in the extraction process, it not only causes loss of extractant, but also brings environmental pollution. In order to solve this problem, researchers graft or synthesize it onto a solid carrier, and then use it to adsorb and separate metal ions, which can prevent the dissolution loss of the extractant and protect the environment. Grad *et al.* [53] used dibenzo-18-crown-6 ether to functionalize Amberlite XAD7 polymer and obtained a new adsorption material. The presence of the CE on the polymer surface was evidenced by the characterization of the obtained material by X-ray energy dispersion (EDX), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). Evaluation of the thermodynamic parameters from the van't Hoff equation indicated that the studied adsorption process was a spontaneous and endothermic one. The newly produced adsorbent material (XAD7-DB18C6) had a maximum adsorption capacity of Pd(II) IS 6.5 $mg \cdot g^{-1}$. Dave *et al.* [54] synthesized a new type of sorbing material by immobilizing monoaza dibenzo18-crown-6 ether on modified Amberlite XAD-4 beads and was used to extract rare earths. The result shows that the preconcentration factor of La(III) is 120, Nd(III) is 131, and Sm(III) is 151. The adsorption rate are very fast with a loading half time ($t_{1/2}$) of less than 10 min.

2.1.2. 15-Crown-5

15-Crown-5 is a CE consisting of 15 atoms in its cyclic structure, including 5 oxygen atoms and 10 carbon atoms (as shown in Fig. 2(b)). It is often used for the extraction and separation of transition metal ions due to its cavity size, which closely matches the ionic radii of most transition metals. Bezdomnikov et *al.* [55] conducted a detailed study on the extraction of Li^+, Na^+ and K^+ perchlorates from chloroform using benzo-15-crown-5 (B15C5). It has been shown that the use of $LiClO_4$ during the extraction process can prevent the accumulation of K^+ and reduce the loss of extractant. Interestingly, lithium perchlorate was found to be extracted as a complex with an atypical ratio of Li/CE ratio of 1:2. The anhydrous complex $[Li(B15C5)(ClO_4)]$ and $[Li(B15C5)_2(H_2O)](ClO_4)$ were characterized by X-ray and FT-IR spectroscopy. A comparative analysis of the spectra confirmed the unique structure of the extracted lithium complex.

Xu *et al.* [56] proposed a promising liquid–liquid extraction system using extractants, 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), and thia-benzo-15-crown-5 (TB15C5), for the selective recovery of indium (In^{3+}) from the leaching solution of end-of-life liquid crystal displays (LCDs). The results showed that the complexation affinity of the CEs for In^{3+} followed the order 15C5 > B15C5 > TB15C5. The mechanism of CEs bonding with In^{3+} and Sn^{2+} by computational modeling (as shown in Fig. 3). It is clearly seen that In^{3+} lies exactly in the plane of the oxygen atoms of 15C5 and B15C5, because the ionic diameter of In^{3+} (0.162 nm) fits well the cavity size of the two CEs (0.172–0.184 nm).

Sun *et al.* [57] synthesized benzo-15-crown-5 ether (B15C5) and investigated its use as a lithium extractant. The selectivity of B15C5 for Li^+ was examined through both experimental studies and density functional theory (DFT) calculations. Under the experimental conditions of pH 6.0, temperature of 30 °C and extraction time of 2 h, the extraction efficiency of Li^+ reached 37 %, significantly higher than that of potential impurity ions such as Co^{2+}, Ni^{2+} and Mn^{2+}. B15C5 can preferentially bind to Li^+ in solution. The calculated values are aligning well with the experimental results.

Zubenko et *al.* [58] synthesized benzodiazepine 15-crown-5 using 1,2 bis(2-iodoethoxy) benzene and diethyl 1,2-phenylbenzene (oxygen) diacetate, and used its affinity of nitrogen and oxygen groups to adsorb Pb^{2+}. In this experiment, the potentiometry and NMR were used to evaluate the binding capacity of CE to Pb^{2+}. The results found that the two-step scheme of preparing benzo-nitrogen ether compounds through reduction of benzo-nitrogen precursors provided a better yield. Furthermore, the rigidity of the benzene ring also contributed to the stability of the combined product.

Wu *et al.* [59] studied the selective extraction of low-concentration light rare earths by 1,7-diaza-15-crown-5 ether (2N15C5) from complex ammonium sulfate solutions containing multiple impurity ions. Liquid–liquid extraction experiments showed that impurity ions affected the extraction distribution of light rare earths by inducing the formation of rare earth ammonium sulfate compound salts, and the single-stage extraction coefficients of light rare earths were 2.20 for aluminum (Al^{3+}) and 7.80 for iron (Fe^{3+}) under the condition of pH 1.5±0.5 and $[SO_4^{2-}]_T/\sum Ln^{3+}<10$. Multistage counter-current extraction can further enhance the selective extraction of light rare earths with $\beta_{LREs/Al}=21.41$ and $\beta_{LREs/Fe}=23.33$ from the tail liquid wastewater. Density functional theory calculations indicated that steric hindrance caused by size compatibility and electron density-based weak interactions affected the coordination between 2N15C5 and different cations.

2.1.3. 12-Crown-4

12-Crown-4 is a CE with 12 atoms in its cyclic structure, consisting of 4 oxygen atoms and 8 carbon atoms (as shown in Fig. 2(c)). 12-Crown-4 generally have cavity sizes in the range of 0.12 to 0.18 nm, and have good selectivity for lithium with an ion diameter of about 0.14 nm [60]. As a result, it is often used as an excellent chemical reagent for the separation lithium ion. However, due to the flexibility of its ring structure, significant deformation occurs when it complexes with metal ions, which hinders desorption and compromises the stability of the complexes. To enhance the stability of 12-crown-4 complexes with metal ions, rigid benzene ring or long-chain alkyl with steric blocking effects are often introduced.

Mashahadizadeh *et al.* [61] studied the transport of Au(III) ions through a chloroform bulk liquid membrane using tetrathia-12-crown-4 as a specific ion carrier. The results indicated that Au(III) was quantitatively transported across the liquid membrane, with thiocyanate serving as a suitable stripping agent in the receiving phase. After 90 min, the amount of gold transported reached (99 ± 2)%. Furthermore, they observed that gold ions have excellent selectivity relative compare to a wide range of alkali, alkaline earth, transition and heavy metal ions.

Bai *et al.* [62] synthesized 2-(allyloxy) hydroxymethyl-12-crown-4-ether (2AM12C4) by functionalizing polymer brush (PVBC-*g*-PCE) on a macroporous polymer high internal phase emulsion (PolyHIPE) for the selective recovery of Li^+ (the synthesis process is shown in Fig. 4). The results found that the grafted polymer brush of 2AM12C4 was the driving force behind the improved the bonding performance. PVBC-*g*-PCE exhibited high physical strength, a high density of accessible binding sites, and large permeability gap. The maximum monolayer binding capacity of PVBC-*g*-PCE was 4.43 $mg \cdot g^{-1}$. In the presence of four interfering ions (Na^+, K^+, Mg^{2+} and Ca^{2+}), the selectivity separation coefficient (α) of Li^+ is 3.16–7.98, The results demonstrated that PVBC-*g*-PCE, with its abundant and accessible specific recognition sites, can be an effective adsorbent for Li^+ separation.

Generally speaking, when the single CE is used as the extractant, the separation and recovery of valuable metal ions are different due

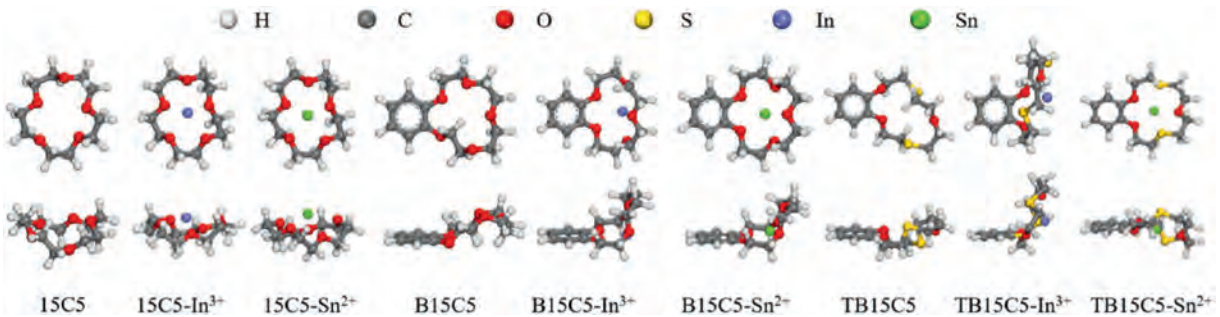

Fig. 3. Optimized structures of 15C5, B15C5 and TB15C5, and their complexes with In^{3+} and Sn^{2+} [56].

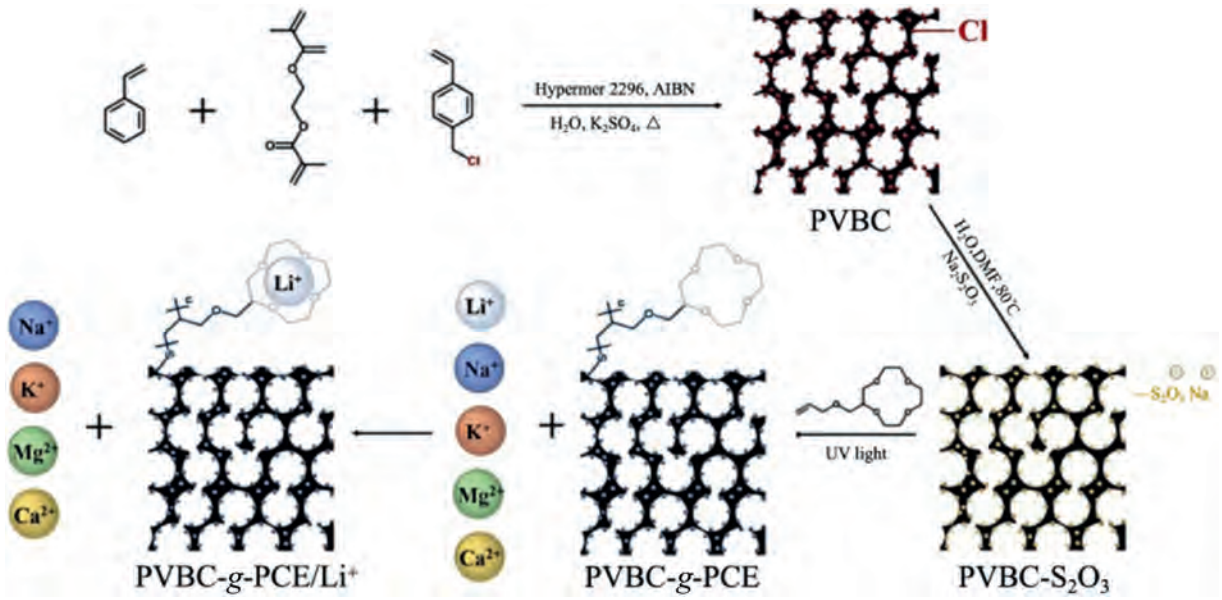

Fig. 4. Synthesis process of PVBC-*g*-PCE [62].

to the structure of CE. 18-Crown-6 is typically employed for the extraction and separation of metal ions with larger ionic radii, such as Cs^{+}, Rb^{2+} and Sr^{2+} [63–65]. 15-Crown-5, with a slightly smaller cavity, is more suitable for separating most transition metals; and 12-crown-4 is widely utilized in the separation and extraction of lithium ions. With the development of technological advancements, researches on the extraction and separation of valuable metal ions using these three CEs and their derivatives are no longer limited to traditional beaker experiments, but has incorporated many applications of computer technology, such as density functional theory (DFT) calculations [66,67], and natural bond orbital (NBO) analysis [68,69]. These technologies have allowed for deeper investigation into the structure of extractants, reaction energy changes, and various reaction mechanisms, thereby expanding the potential applications of CEs.

2.2. Synergistic extraction system

The extraction of valuable metal ions from aqueous solutions using single CEs has certain limitations. Therefore, one or more extractants with CE are mixed together, or the ions or functional groups are introduced into the CE to regulatory the structure for enhancing extraction efficiency through the synergistic extraction mechanism [70–72]. In this paper, various synergistic extraction systems are reviewed, including multi-extractant systems and ionic liquid synergistic systems, categorized based on their underlying synergistic mechanisms.

2.2.1. Multiple extractant system

In the multi-extractant system, the CE extractant is mixed with two or more other extractants, each extractant directly participates in the reaction with metal ions, and improves the separation ability of organometallic ions through the co-extraction effect. Sahu *et al.* [73] studied the extraction of thorium(IV) and uranium(VI) from nitric acid solutions using mixtures of 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) and various ether crowns, including dicyclohexano-18-crown-6 (DC18C6), benzo-18-crown-6 (B18C6), dibenzo-18-crown-6 (DB18C6) or benzo-15-crown-5 (B15C5). The results found that these metal ions were extracted into chloroform as $Th(PBI)_4$ and $UO_2(PBI)_2$ when HPBI was used alone, and as $Th(PBI)_4$-CE and $UO_2(PBI)_2$-CE in the presence of CEs. The binding affinity of $Th(PBI)_4$ and $UO_2(PBI)_2$ to CE follows the basicity sequence of the CE, although steric effects became more prominent with DC18C6 and DB18C6. While the CE exhibited synergistic behavior in these extractions, the size fit between the cations and the CE cavities was not a significant factor in these HPBI complexes. Additionally, very high separation factors between uranium(VI) and thorium(IV) were observed when extracted from strongly acid solution using HPBI alone or HPBI + CE systems.

Meguro *et al.* [74] used *β*-diketone (HA) and 18-crown-6 to extract ions of trivalent actinides Am and Cm and ions of lanthanides Nd to Tb in 1,2-dichloroethane solvent. The results found that the metal ion M(III) was extracted through one of two competitive extraction reactions: either a synergistic ion-pair extraction (SIPE) of a cationic complex, $MA_2(18C6)$, or a synergistic extraction (SE) of a neutral complex, $MA_3(18C6)$. Steric hindrances due to the bulkiness of the substituent group of HA influence the predominancy of one of the competitive reactions, SIPE or SE. Large separation factors are obtained by SIPE of M(III) ions using HA with relatively small substituent groups. The steric effect can be interpreted by taking into consideration the configuration of the extracted complexes.

Abdollahzadeh Khanghah *et al.* [75] used an emulsion liquid membrane (ELM) containing dicyclohexano-18-crown-6 (DC18C6) as a carrier and di-(2-ethylhexyl) phosphoric acid (D2EHPA) as a synergistic carrier to optimize the extraction of Ca^{2+}. They found that the optimum values were: DC18C6 concentration at 0.035 mol·L^{-1}, feed phase pH of 4, a feed/emulsion volume ratio of 2.3, and a W/O/W stirring time of 23.4 min. Under the optimal condition, DC18C6 exhibited negligible extract ability, while D2EHPA achieved an extraction efficiency of 62.2%. Combining both carriers, however, significantly increased the extraction efficiency to 97.3%, indicating a synergistic effect that enhanced the extraction of Ca^{2+}. Furthermore, the selectivity of the ELM towards Ca^{2+} was examined in binary solutions of Ca^{2+}/Li^{+}, Ca^{2+}/Na^{+}, and Ca^{2+}/Mg^{2+}. The ELM demonstrated selectivity for Ca^{2+} over Li^{+}, Na^{+}, and Mg^{2+} with separation factors of 4.4, 2.0 and 8.1, respectively. The scheme of the transport mechanism of Ca(II) by synergistic carriers through ELM is shown in Fig. 5.

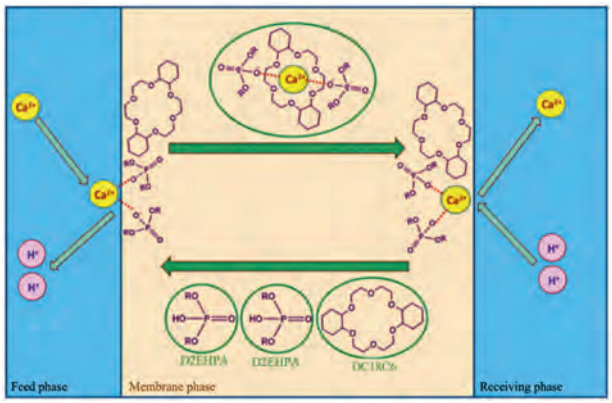

Fig. 5. The transport mechanism of Ca(II) by synergistic carriers through ELM [75].

For multiple extraction system, the proportion of extractants and the conditions during extraction are more important. It needs to adjust the ratios of extractants to achieve the effects of synergistic extraction. In the large-scale industrial application, the high extraction efficiency and stability of the extraction system are also required.

2.2.2. Ionic liquids synergistic system

Ionic liquids (ILs) is an organic salt composed of anions and cations, which has many advantages, such as non-toxic, non-flammable and non-volatile, making it an ideal choice to replace traditional organic solvents when extracting and separating metal ions, and has become a research hotspot in recent years [76]. In recent years, the combination of ILs with CEs for the coordinated extraction of metal ions has become a new research field.

Houzar *et al.* [77] studied the extraction of strontium from nitric acid (HNO_3) solution using ILs as a synergist and CE as an extractant. The results found that the efficiency of strontium in the following order: dibenz-18-crown-6 < benz-15-crown-5 ≈ 18-crown-6 < di-*tert*-butyl-dicyclohexano-18-crown-6 ≈ dicyclohexano-18-crown-6. Zhang *et al.* [78] conducted an experiment using dibenzo-15-crown-5-ether as an extractant, ILs as a co-extractant, and anisole as a diluent to separate lithium isotopes *via* an organic liquid membrane system (depicted in Fig. 6). Their experimental results demonstrated that the combination of the CE extractant with lithium ions, as well as the exchange of lithium isotopes, was a spontaneous exothermic reaction. This finding confirmed the efficiency and effectiveness of this extraction system in selectively separating and extracting lithium isotopes. Liu *et al.* [79] investigated the use of 4-aminobenzo-15-crown-5 (4-NH_2-B15C5), 4-nitrobenzo-15-crown-5 (4-NO_2-B15C5), and benzo-15-crown-5 (B15C5) as extraction agents within a green and efficient ILs–anisole system to separate lithium isotopes. The results revealed that the molar ratio of CE to lithium ion in the complex was 2:1. In terms of extraction performance, 4-NH_2-B15C5 showed the highest extraction efficiency, followed by B15C5 and then 4-NO_2-B15C5.

In conclusion, the extraction systems of CE hold great promise for future applications due to its advantages, including high extraction efficiency, rapid extraction rate, minimal dissolution loss and environmentally friendly characteristics. However, CEs have certain toxicity and water solubility. Once released into the environment, CE will cause serious environmental pollution [80]. A method of fixing CE, such as loading CE onto a solid substrate, must be developed to prevent its harmful entry into the environment. In addition, the extraction systems usually are more complex. It is necessary to control various influencing factors more strictly in the application process. So the cost of synthesis and modification of CE is very high. Reducing its cost in the future is a top priority.

3. Influencing Factors

Many studies are devoted to exploring the influencing factors on the extraction and separation of metal ions by CEs. The influencing factors mainly include the properties of the organic phase and aqueous phase.

3.1. Properties of organic phase

In the organic phase, the type and concentration of CEs, the properties of synergists and diluents all have important effects on the extraction efficiency.

3.1.1. Concentration and structure of CE

CEs as extractants conform to the general extraction equilibrium. Generally, the extraction rate and efficiency increase with the

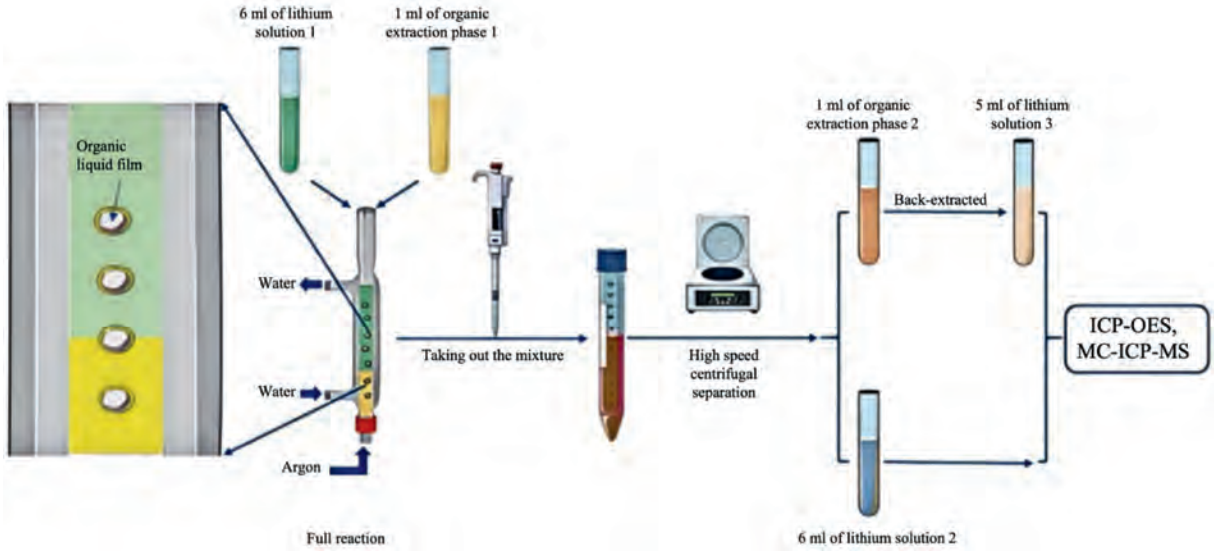

Fig. 6. Ionic liquids assist anisole in the extraction of lithium ions [78].

concentration of CE. However, the stability and stoichiometric ratio of the complex are related to the relative size of the metal ion and the 'hole' of the ring. If the ionic diameter of the metal ion fits precisely into the hole of the cyclic ring, a stable 1:1 complex can be formed. However, if the metal ion is too small to fit the ring, this may lead to incomplete complexation or the formation of 2:1 and even 3:2 (M:L) stable complexes. Similarly, a metal ion of relatively large size may form 1:2 or 2:3 complexes [81]. Zhao *et al.* [82] provided a comparison of the diameters of different alkali metal ions and several common CE pore diameters (as shown in Table 1). The structure of CEs also has a significant influence on the extraction and separation of valuable metal ions, particularly the ring itself and certain hybrid modifications, such as the side-chain structure of the CE.

Zhu [83] studied the relationship between the concentration of CE and the partition ratio of lithium ions by calculating the chelate configuration in an experiment on the separation of lithium isotopes using ILs-assisted AcB15C5. After data fitting, it was found that the slope of the linear plot was 0.97014, which is approximately 1. This indicates that the binding ratio of lithium ions to CE is 1:1. GaussView software was further used to compare the stability of the two configurations, 1:1 and 1:2, and the results confirmed the above conclusion—namely, that the concentration of CE is proportional to the lithium extraction efficiency.

Regarding the structure of CEs, Xiong *et al.* [84] used dibenzo-14-crown-4 ether functionalized with an alkyl C16 chain (DB14C4-C16) as an extractant to selectively recover lithium from brine. It was found that adding two benzene rings to 14C4 enhances the rigidity of the CE, maintains the cavity size, and minimizes energy loss during the complexation process. The long lipophilic C16 alkyl chain effectively reduces the dissolution loss of the CE in the aqueous phase and increases the extractant load in the organic diluent, thereby improving the lithium extraction efficiency of the solvent extraction system.

Nesterov and Zakurdaeva [85] modified dibenz-14-crown-4 (DB14C4) by introducing branched alkyl substituents to improve the solubility of macrorings in the organic phase, while reducing their solubility in the aqueous phase. In addition, the extraction efficiency of lithium ions can be improved by increasing the basicity of polyether oxygen atoms, as shown in Fig. 7.

Wang [86] used 4-nitrobenzo-15-crown-5 (4-NO_2-B15C5), 4-aminobenzo-15-crown-5 (4-NH_2-B15C5), and benzo-15-crown-5 (B15C5) as extractants to study the effects of CEs with different side chains on the extraction and separation of lithium isotopes. The results showed that the extraction efficiency of CEs at the same concentration follows the order: 4-NH_2-B15C5 > B15C5 > 4-NO_2-B15C5 (as shown in Fig. 8). According to the CE structure (as shown in Fig. 9), this phenomenon can be explained by the fact that the strong electron-donating groups increase the charge density on the carbon–oxygen ring of the CE, enhance the ion-dipole interaction between the CE ring and lithium ions, an thus increase the binding ability of the CE to lithium ions. Conversely, the strong electron-withdrawing side chains reduce the charge density on the carbon–oxygen ring, inhibit the ion-dipole interaction and decrease the binding ability of the CE with lithium ions.

Table 1
Comparison of different alkali metal ion diameters and pore diameters of several CEs [82].

Types of ionst	Diameter/nm	Types of CEs	Diameter/nm
Li^+	0.120	12-C-4	0.120
Na^+	0.190	15-C-5	0.170–0.220
K^+	0.266	18-C-6	0.260–0.320
Rb^+	0.296	14-C-4	0.120–0.150
Cs^+	0.344	B15-C-5	0.170

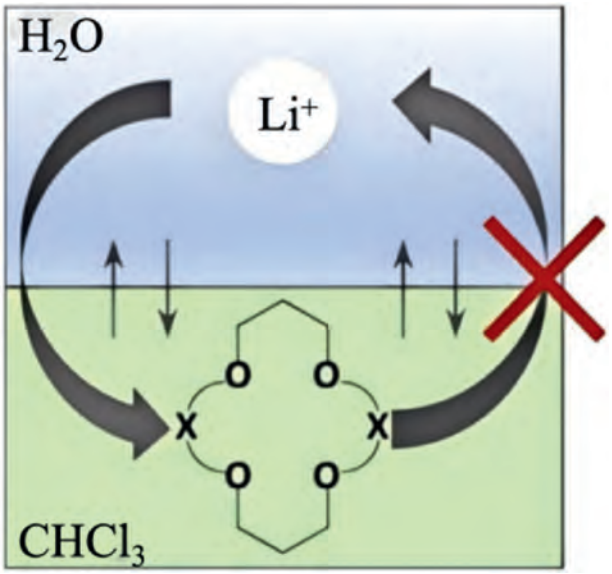

Fig. 7. The introduction of long-chain alkyl groups reduces the water solubility of CEs [85].

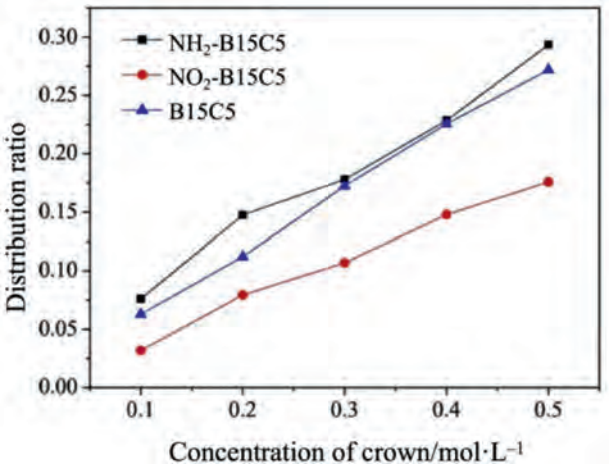

Fig. 8. Lithium extraction rate of lithium by CEs with different side chains [86].

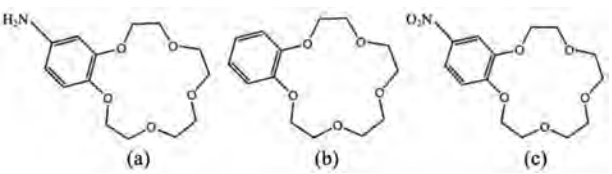

Fig. 9. Structural formulas of (a) 4-NH_2-B15C5, (b) B15C5 and (c) NO_2-B15C5 [86].

Ciopec *et al.* [87] used dibenzo18-crown-6 (DB18C6) and dibenzo 30-crown-10 (DB30C10) modify the magnesium silicate surface for palladium recovery from waste water. The inorganic support $MgSiO_3$ before and after functionalization with the two CEs were characterized by the scanning electron microscopy (SEM). The results showed that the materials have specific surfaces and different pore volumes because of the different size and structure of the CEs. The mechanism of adsorption process was studied that the complexation of two molecules of Pd(II) in a molecule of DB30C10, confirmed by the higher adsorption value (~34.7 $mg \cdot g^{-1}$)

compared to $MgSiO_3$-DB18C6 (~20 $mg \cdot g^{-1}$), where the CE DB18C6 allows only one molecule of Pd(II) to be complexed.

3.1.2. Properties of co-extractant and diluent

The co-extractant and diluent in the organic phase also affect the extraction efficiency. They influence the ability of CEs to adsorb and separate valuable metal ions by forming a synergistic extraction system or by improving the viscosity and solubility of the system.

Hua *et al.* [88] used tributyl phosphate (TBP) and di(aminobenzo)-14-crown-4 (CE) as extractants, $[C_4mim][NTf_2]$ (IL) as a co-extractant, and methylene chloride as a diluent to form a highly efficient solvent extraction system for selective Li^+/Mg^{2+} separation. The results showed that under optimal extraction conditions with 20 $mg \cdot ml^{-1}$ CE and 0.61 $mmol \cdot ml^{-1}$ IL, the maximum single-stage Li extraction efficiency of the TBP—CE—IL system were 89.5% and 81.8% for Mg/Li mass ratios of 3.5 and 70, respectively. The Li/Mg separation factors reached 515 and 422. Compared to the TBP—IL system, the addition of CE significantly improved both the Li extraction efficiency and Mg—Li selectivity. This improvement was attributed to the hydrogen bond interaction between CE and TBP/IL, as well as the cavity size effect between CE and Li, which enhanced CE coordination and increased the stability of the complex formed in the organic phase. Wang and Zhuang [89] used a type of calixarene functionalized with CE to extract cesium, demonstrated higher cesium selectivity compared to CE alone. Additionally, the system was stable in acidic media and could be easily stripped from the solvent using water or dilute nitric acid solution.

Zhang *et al.* [90] introduced three types of ILs with different anions—1-hexyl-3-methylimidazolium tetrafluoroborate, 1-hexyl-3-methylimidazolium hexafluorophosphate, and 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide—into the extraction system for lithium ion isotopes using CE bromide to study their extraction performance, strengthening mechanisms, and micro-interface structure. The study identified ILs that could enhance the system's extraction performance without significantly extracting lithium ions, offered technical support for the selection of ILs in the separation of other metal ions.

3.2. Properties of aqueous phase

The aqueous phase conditions in the process of extracting metal ions with CEs mainly include the anion effect, solvation effect, type of metal ions and pH value. These factors usually do not affect the extraction efficiency alone, but are combined, and two or three factors affect the extraction process simultaneously.

3.2.1. Effect of anion

The extract formed by the extraction of valuable metal ions using CEs enters the organic phase as ion pairs (ML^+A^-). Extraction as an ion pair has significant advantages over extraction as a molecule in terms of improving extraction efficiency and selectivity [81]. Consequently, the properties of the anion greatly affect the solubility of the extract in the organic phase. While ion pairs formed with common inorganic salt ions have low solubility in the organic phase, those formed with larger anions, such as picric acid and dipicrylamine, exhibit greatly enhanced solubility. Organic acid ions are generally more favorable for the extraction of metal ions by CEs than inorganic acid ions. The greater the hydrophobicity of the organic acids is, the higher the extraction capacity of the system is, as demonstrated by the order: picrylamine > picric acid > dinitrophenol. The extraction ability of inorganic anions for alkali metal ions follows the order: $ClO_4^- > I^- > NO_3^- > Br^- > OH^- > Cl^- > F^-$.

Wang *et al.* [86] used ionic liquid and benzyl ether as co-extractant and solvent, CE as the extractant to establish a green and efficient extraction separation system for lithium isotopes. The results indicated that lipophilic cations are formed between CE and Li^+ at the interface of the two phases, and that the anion in the lithium salt solution affects the binding of CE to the lithium ion. As shown in Table 2, the order of single-stage separation coefficients and the abundance values of ^6Li is the same: CF_3COOLi > LiI > LiBr > LiCl. This order can be reasonably explained by the soft-hard acid-base theory: the larger the anion radius of the lithium salt is, the greater the softness is, resulting in a higher single-stage separation coefficient and abundance value of ^6Li.

Tsebrikova *et al.* [91] studied the effect of counterion A on the solid-state molecular structures and stability constants in solution for the complexes of MA_2 salts (M = Co^{2+}, Ni^{2+}, Cu^{2+}; A = ClO_4^-, NCS^-, NO_3^-) with phosphorylated cyclen and diaza-18-crown-6 derivatives. This research reported the synthesis of the complexes and determined the solid-state molecular structure of eight new complexes by X-ray diffraction, IR and electronic absorption spectra. The stability constants of cobalt(II) complexes with 1,4,7,10-tetrakis [(diphenylphosphoryl)methyl]-1,4,7,10-tetraazacyclododecane (L^1) in acetonitrile were estimated. It was found that the counter ions in MA_2 salt had significant influence on the structure and stability of the complex. The salt anion affected both the number of complexes and the stability of complexes.

3.2.2. Effect of solvation

Hydrocarbons and chloroalkanes are commonly used as solvents for CEs to extract and separate valuable metal ions. The polarity of the solvent significantly affects its selectivity. CE complexes are of the ionic association type and possess some polarity, making their solubility in polar solvents better than in non-polar solutions. Currently, $CHCl_3$ and CH_2Cl_2 are generally used as solvents.

Kuz'mina *et al.* [92] studied the solvation of dibenzo-18-crown-6 ether in water-aprotic solvent mixtures. In this experiment, the Gibbs free energies of dibenzo-18-crown-6 ether from dimethyl sulfoxide and *N*,*N*-dimethylformamide to their mixtures with water ($\Delta_{tr}G^0(DB18C6)_{solv} \rightarrow \chi_w$) were determined using the phase distribution method. The enthalpies of dissolution of DB18C6 were measured by calorimetry at 25.00°C ± 0.01 °C. An analysis was conducted on the influence of solvent composition and properties on the thermodynamic characteristics of DB18C6 solvation. The results showed that the solvent composition had no significant effect on the solvation state of the CE. Additionally, a compensation effect in the enthalpy and entropy contributions to $\Delta_{tr}G^0(DB18C6)$ was observed. It was found that the primary contribution to the change in the thermodynamic characteristics of DB18C6 solvation arises from the resolvation of the crown ring oxygen atoms, which occurs at $\chi_w > 0.6$ mol.

Jóźwiak *et al.* [93,94] studied the effect of temperature on the solvation process of CE 15C5 in mixtures of water—ethanol, water—propanol-1—alcohol, and water—methanol. The temperature's impact on the preferential solvation of 1,4-dioxane and 12-crown-4 ethers in mixtures of water with formamide was also

Table 2
Unipolar separation coefficient and enrichment degree of lithium salts [86].

Lithium salt type (1 $mol \cdot L^{-1}$)	Single-stage separation factor	The enrichment of ^6Li
LiCl	1.0328	7.752
CF_3COOLi	1.0362	7.788
LiBr	1.0337	7.760
LiI	1.0338	7.770
$LiClO_4$	1.0325	7.752
$LiNO_3$	1.0354	7.776

studied [95]. The results showed that lower temperatures enhance the preferential solvation of 15C5 molecules by water or alcohol molecules. As the temperature increases, the kinetic energy of the molecules rises, weakening the interactions involved in preferential solvation.

3.2.3. Types of metal ions

The radius and charge of metal ions affect not only their electrostatic interactions with CE but also the hydration. Consequently, ions with smaller radii and higher charges, such as Li^+ and Ca^{2+}, are more difficult to extract than Na^+. DB18C6 exhibits similar extraction abilities for Ti^+ and K^+ ions, but very low extraction ability for Ti^{3+} ions. Additionally, when comparing the extraction performance of DB18C6 for Pb^{2+} and Sr^{2+}, it is found that the extraction capacity for Pb^{2+} is 40–50 times greater than that for Sr^{2+}, while the difference in complexing capacity is only 5–6 times. This discrepancy is attributed to the strong hydration of CE complexes, making it difficult to extract them into organic solvents. Moreover, metal ions with different electron configurations require different coordinating atoms. For example, replacing the oxygen atom in CE with a sulfur atom enhances extraction performance for soft metal ions such as Ag^+ and Hg^+ [96].

Cao *et al.* [97] utilized density functional theory to systematically calculate the coordination of four CEs (9C3, 12C4, 15C5, and 18C6) with metal ions, using ethylene glycol dimethyl ether (DME) as a model compound. The results showed that the energy barrier in the DME conformation can be reduced by combining with metal ions, and that the greater the charge-to-radius ratio of the combined metal ions, the greater the reduction in this energy barrier. The isotope effect of metal ion coordination with CE is primarily determined by the relative mass difference of the metal isotopes and the bond length of the coordination bond, and is also related to the conformation of the CE. For the same metal ion–CE complex, the complex formed with the heavier isotope exhibits lower free energy. For example, for ^7Li and ^6Li, the Li-2222 complex of the Li-12C4 coordination shows the largest isotopic effect.

Zheng and Chen [98] calculated the extraction constants of picric acid for common CEs and metal ions according to the 'optimum theory' providing a straightforward reference for selecting suitable CEs. The data are shown in Table 3.

3.2.4. Effect of pH value

In the process of metal ion separation by CE extraction, H^+ ions in water phase usually compete with metal cations for the oxygen atom donor groups. Therefore, adjusting the pH to a neutral range during the extraction and separation process can weaken the competition between metal ions and H^+, while also preventing the formation of metal hydroxides. Additionally, appropriate pH conditions can further enhance the extraction and separation efficiency of CE for valuable metal ions in various aspects.

Xiong *et al.* [84] synthesized dibenzo-14-crown-4-16 carboalkyl using an ion imprinting method to separate lithium from brine containing metal elements such as sodium, magnesium, iron, and lithium. During the optimization of extraction conditions and testing the effectiveness of the method in salt lake water, it was found that pH of 7 provided the optimal conditions for extracting lithium with the synthesized extractant. This confirmed both the practicality of the extraction method and the validity of the underlying theory.

Strzelbicki *et al.* [99] utilized sym-(decyl)dibenzo-16-crown-5-oxyacetic acid (1) and sym-(decyl)dibenzo-16-crown-5-oxymethylphosphoric acid monoethyl ester (2) as ion carriers for the selective transport of alkali metal cations through polymer-supported liquid membranes (PSLM). The influence of aqueous pH on the infiltration of metal cations was studied. The results showed that Na^+ permeation increases with decreasing acidity for both ionophores. In the pH range close to neutral solutions, the Na flux reached a plateau region, where it remained virtually constant despite the increasing pH.

To sum up, the properties of both the aqueous and organic phases play crucial roles in the extraction and separation of valuable metal ions using CE. During the complexation process between CE and metal ions, it is essential to identify the most suitable extraction conditions through repeated experiments [100].

4. Conclusions and Future Prospectives

The separation and extraction of metal ions by using CE as extractant has made great progress in extraction system, extraction efficiency and extraction capacity. The single extractant, such as 18-crown-6 (18C6), 15-crown-5 (15C5), 12-crown-4 (12C4), all can selectively extract metal ions. In order to further enhance extraction efficiency and extraction capacity, scholars have made many attempts on regulating the structure of CE extractants by modification with special functional groups or mixing one or more extractants with CE. The extraction mechanism also was deeply analyzed. Especially, with the advancement of big data and computational tools, the calculation of coordination energy based on mathematical models of CEs provides a simple and rapid classification method for complex conformation issues in the theoretical study of metal ion complexation. The influencing factors mainly include the properties of the organic phase and aqueous phase. The properties of organic phase, the type and concentration of CEs, the properties of synergists and diluents all have important effects on the extraction efficiency. In addition, the aqueous phase conditions in the process of extracting metal ions with CEs mainly include the anion effect, solvation effect, type of metal ions and pH value. This technology plays an important role in the field of metal ion separation because of its unique advantages. However, the use of CE and its extraction system to extract metal ions still has some problems in practical application. The main problems are that the price of CE is relatively high, the water solubility is serious, and the certain toxicity of CEs are easy to cause environmental pollution. Therefore, further researches on synthesis and modification of CEs should be carried out to further improve the selectivity of metal ions and reduce the cost of synthesis or modification. By developing solid matrix materials of CEs, the loss of water solubility and toxic pollution of CE can be reduced and the utilization efficiency of CE

Table 3
lgK_{ex} values of CE and picric acid metal salt complexes [98].

CE	Li^+	Na^+	K^+	Rb^+	Cs^+	Ag^+	Tl^+	Ca^{2+}	Sr^{2+}	Ba^{2+}	Hg^{2+}	Pb^{2+}
12C4	0.77	0.95	0.57	0.29	0.21	1.96	2.22	–	–	–	–	–
15C5	1.29	3.90	2.58	2.14	1.90	4.45	3.80	3.72	5.70	5.20	–	6.46
B15C5	1.26	3.29	1.93	1.44	1.08	3.33	3.23	–	–	–	–	–
18C6	1.92	3.39	5.97	5.43	4.38	4.44	6.30	7.03	9.72	9.72	7.97	11.75
DB18C6	–	2.10	4.65	3.75	3.07	3.56	4.49	4.01	5.38	–	6.22	7.16
DB24C8	0.67	2.05	2.79	3.00	3.15	3.09	4.06	3.07	3.99	6.86	–	6.32

can be improved. In short, the above problems must be solved in the future to realize the industrial application of CE in the field of metal separation and recovery.

CRediT Authorship Contribution Statement

Jie Liu: Writing – review & editing, Writing – original draft, Conceptualization. Xin Zhang: Data curation. Xingjie Lu: Investigation. Qianting Li: Supervision, Data curation. Zhixiao Xue: Methodology, Investigation, Conceptualization. Qiulu Zhang: Supervision, Resources. Guizhi Wu: Validation, Supervision, Conceptualization. Wenxiang Xia: Formal analysis, Data curation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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