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Benzo-12-crown-4-ether-mediated lithium transport in supercritical CO₂: A preliminary study for recycling lithium-ion battery cathode materials

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ABSTRACT

The design of metal-complexing copolymer architectures is essential to enable solvent-free recovery of critical metals, and of interest for a large number of applications. In this study, the lithium transport efficiency of benzo-12-crown-4-ether (B12C4) from various salts (LiNO₃, LiOAc, Li₂SO₄ and Li₂CO₃) in supercritical carbon dioxide (scCO₂) was investigated. Among these salts, only Li⁺ from LiNO₃ was effectively complexed by B12C4 in scCO₂. As both B12C4 and the [B12C4-Li]NO₃ complex are poorly soluble in scCO₂, a scCO₂-philic gradient polymer, poly(B12C4 ethyl methacrylamide-*grad*-1,1,2,2-tetrahydroperfluorodecyl acrylate) [P(B12C4EMAAM-*grad*-FDA)] was synthesized by RAFT polymerization. In this copolymer, the FDA unit is CO₂-philic, while B12C4EMAAM acts as a metal-complexing group. The solubility of the copolymer was determined by cloud point measurement and compared to that of a PFDA homopolymer. The lithium recovery yield from lithium nitrate, quantified by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis, reached 83 % under supercritical conditions (40 °C and 250 bar) in the presence of a small amount of water (molar ratio [water]/[LiNO₃]=7.6), whereas only 25 % was recovered under dry conditions. The Li⁺ transport efficiency of the copolymer was also evaluated in the presence of cobalt ions. Using a mixture of lithium nitrate and cobalt nitrate hexahydrate (molar ratio [B12C4EMAAM]:[Li]:[Co]=3.6:1:1), recovery yields of 46 % and 84 % for lithium and cobalt were obtained, respectively. Despite its lack of selectivity toward lithium, P(B12C4EMAAM-*grad*-FDA) demonstrates strong potential as a complexing ligand for both lithium and cobalt under scCO₂ conditions.

1. Introduction

The demand for critical metals (e.g., lithium, cobalt, nickel, and manganese) is increasing due to the global shift toward electrification in the automotive sector. The criticality of these resources is expected to intensify as European policies advance the transition from internal combustion (IC) engines to electric vehicles (EVs). This transformation is beneficial for reducing carbon footprints, achieving climate goals and accelerating the transition to clean energy. Lithium-ion batteries (LIBs) have emerged as the preferred energy storage technology due to their high energy density, long cycle life, and relatively low weight. LIBs typically reach end-of-life (EoL) status after about ten years, generating significant volumes of waste that must be properly managed to prevent

environmental contamination. Notably, lithium recovery from spent LIBs is considerably more efficient than extraction from primary sources: approximately one ton of lithium can be reclaimed from just 28 tons of EoL LIBs, compared to about 250 tons of mineral ore or 750 tons of lithium-rich brine required for equivalent production [1].

Cathode materials in EV batteries include LiCoO₂ (LCO), LiNi_xMn_yCo_zO₂ (NMC, $x + y + z = 1$), LiFePO₄ (LFP), LiMn₂O₄ (LMO), and LiNi_xCo_yAl_zO₂ (NCA, $x + y + z = 1$) [2]. In general, the typical ranges of elemental composition of LIB cathode material are 6–60 wt % for Co, 20–50 wt % for Ni, 6–20 wt % for Mn and 7 wt % for Li. Improper disposal of these batteries results not only in environmental contamination, but also in the loss of valuable metal resources, underscoring the need for sustainable recycling solutions.

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Hydrometallurgy and pyrometallurgy are the most common conventional methods for recovering critical metals from waste LIBs [3]. Hydrometallurgy is the most efficient method to date, enabling the production of battery-grade metal precursors through acid leaching (organic and inorganic) [4–7], alkali leaching [8], solvent extraction [9, 10], and selective precipitation [9]. However, this approach involves high chemical consumption, significant wastewater generation, and complex multistep processes [2].

Supercritical fluid extraction (SFE) has recently emerged as an alternative to overcome some limitations of hydrometallurgy. In particular, supercritical carbon dioxide (scCO₂) offers tunable solvating power, non-toxicity, and ease of separation from extracted materials, making it an environmentally friendly option [11]. ScCO₂-based extraction has been applied in various sectors such as food industries [12], pharmaceuticals [13], rare earth metal recovery [14], textile processing [15], heavy metal extraction [16] and recently extraction of metals from spent LIBs [17]. However, its use for critical metal recovery remains limited due to the low solubility of complexing ligands and their metal complexes in scCO₂.

The efficiency of SFE is governed by the solubility of both the complexing agent and the corresponding metal complexes [18]. Bertuol *et al.* [19] showed that scCO₂-assisted leaching of LIB cathode materials using aqueous H₂SO₄ + H₂O₂ significantly reduces reaction time from 60 to 5 min using half concentration of the reducing agent (4 vol % of H₂O₂ 30 % instead of 8 vol %) compared to conventional leaching. However, such a process remains a hydrometallurgical method rather than a true scCO₂ extraction, as it implies the presence of an aqueous H₂SO₄ phase, insoluble in scCO₂. Baek *et al.* [14] reported that tributyl phosphate-nitric acid adducts (TBP-HNO₃) can stabilize metal complexes in scCO₂, although the solubility of the adducts and the extraction efficiency are highly sensitive to small variations in the composition, thus compromising its practical application. Similarly, Zhung *et al.* used the TBP-HNO₃ adduct in scCO₂ to extract rare earth metals from fluorescent lamp waste [20], as well as to recover critical metals (Li, Co, Ni and Mn) from spent LIBs [17]. Even though extraction efficiencies as high as 89 % Li, 90 % Co, 90 % Mn and 89 % Ni could be obtained from spent LIBs, the thermal instability of the Li-TBP-HNO₃ complex in scCO₂, leading to reduced coordination efficiency, and the need of HNO₃ undermine the green chemistry advantages associated with scCO₂.

To address solubility challenges, Vauloup *et al.* synthesized a copolymer, poly(1,1,2,2-tetrahydroperfluorodecylacrylate-co-vinylbenzylphosphonic diacid) [P(FDA-co-VBPDA)], which combines leaching, complexation, and solubilization functions within a single architecture [21]. Despite promising extraction yields of up to 75 % for lithium and cobalt, no selectivity between these two metals was observed. This highlights the need for new complexing agents with improved specificity, particularly for lithium recovery.

Macrocyclic ligands such as crown ethers are well-known for their ability to selectively bind metal cations based on the size complementarity between the metal ion and the crown ether cavity [22]. For instance, 12-crown-4 (12C4), benzo-12-crown-4 (B12C4) and dibenzo-14-crown-4 (DB14C4) ethers exhibit high selectivity for Li⁺ ions in the presence of other alkali metals and transition metals, due to the close match between the ionic radius of Li⁺ (60 pm) and the crown cavity size (radius, 50–65 pm) [23–26]. Despite their binding efficiency in polar and aqueous media, the use of crown ethers in scCO₂ systems remains largely unexplored due to the insolubility of the metal-crown ether complexes in this non-polar solvent. Prior efforts to enhance the solubility of crown ethers in scCO₂ have focused either on fluorinated crown ether derivatives (e.g., fluorinated chain containing 14-crown-4 ether, (F14C4) [27]) or on using CO₂-philic counter anions (e.g., pentadecafluoro-n-octanoic acid [28]) leveraging favourable Lewis acid-base interaction between fluorinated chains and CO₂ [29].

Following this approach, Palsdottir *et al.* [27,30] compared the solubility of fluorinated 14-crown-4 ether (F14C4) and methylene 14-crown-4 ether (M14C4) in scCO₂. They also synthesized cation

exchangers (di(2-ethyl-hexyl)phosphoric acid (HDEHP) and tetraethylammonium perfluoro-1-octanesulfonate (TPFOS) to solubilize the metal complex in scCO₂, finding higher solubility for M14C4 (0.30 mol/L at 60 °C and 205 bar) than F14C4 (0.27 mol/L at 60 °C and 285 bar). However, the combination of fluorinated molecules F14C4 and TPFOS showed higher selectivity and extraction efficiency in scCO₂. Similarly, CO₂-philic pentadecafluoro-n-octanoic acid (PFOA) was chosen as a cation exchanger to solubilize crown ether complexes in scCO₂ [28,31].

Interestingly, the use of B12C4 in scCO₂ systems has yet to be investigated, despite its favourable cavity size for Li⁺ complexation. The present work aims to address this gap by employing B12C4 in scCO₂ for lithium extraction from various lithium salts. To improve solubility, a scCO₂-philic gradient copolymer, poly(B12C4 ethyl methacrylamide-*grad*-1,1,2,2-tetrahydroperfluorodecyl acrylate) [P(B12C4EMAAm-*grad*-FDA)], was synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization. In this design, the FDA units ensures CO₂-philicity, while B12C4 enables Li⁺ coordination. As a proof of concept, the transport efficiency of Li⁺ and Co²⁺ from simple salts (LiNO₃, Co(NO₃)₂·6H₂O) was evaluated in scCO₂, avoiding the additional complexity of cathode material leaching. This foundational study aims to demonstrate the potential of B12C4-based architectures for selective lithium recovery and broader applicability to other transition metals in scCO₂.

2. Experimental

2.1. Materials

1,1,2,2-Tetrahydroperfluorodecylacrylate (FDA, BOC Sciences, 98.0 %) was purified by passing it through a fixed bed of activated basic alumina. Azobis(isobutyronitrile) (AIBN, Sigma Aldrich, 98 %) was recrystallized in methanol and dried under vacuum. Benzo-12-crown-4 ethyl methacrylamide (B12C4EMAAm) was synthesized and characterized as shown in the Supporting Information. The chain transfer agent (CTA) 1-(ethoxycarbonyl)-ethyl dithiobenzoate was synthesized according to a previously described procedure [32] (reaction time of 6 h). Poly(1,1,2,2-tetrahydroperfluorodecylacrylate) (PFDA) was synthesized according to the reported procedure (Batch PFDA3 of reference [33]). Benzo-12-crown-4 (TCI, 98 %), lithium nitrate anhydrous (LiNO₃, Thermo Fisher, 99 %), lithium acetate (LiOAc, TCI, 98 %), lithium sulfate anhydrous (Li₂SO₄, Sigma Aldrich, 99.5 % trace metals basis), lithium carbonate (Li₂CO₃, TCI, 98 %), cobalt nitrate hexahydrate ([Co(NO₃)₂·6H₂O], Sigma Aldrich, 98 %), dopamine methacrylamide (Specific Polymers), triethylene glycol di(p-toluenesulfonate) (TCI, 97 %), potassium carbonate (K₂CO₃, Sigma Aldrich, >99 %), anhydrous acetonitrile (MeCN, Sigma Aldrich), methanol (Carlo Erba, Methanol RE-Pure), dichloromethane (DCM, Carlo Erba), trifluorotoluene (TFT) (Sigma Aldrich, anhydrous 99 %), ethyl acetate (EtOAc, Fisher Chemicals, 99 %), magnesium sulfate dried (MgSO₄, VWR Chemicals), and all other chemicals were used as received unless otherwise stated.

2.2. Synthesis of benzo-12-crown-4 ethyl methacrylamide (B12C4EMAAm) monomer

The monomer was synthesized by adapting a procedure already reported in the literature [26], as detailed in the Supporting Information (SI 1).

2.3. Synthesis of P(B12C4EMAAm-*grad*-FDA) copolymer

The P(B12C4EMAAm-*grad*-FDA) copolymer with a targeted molecular weight of 10,000 g/mol at 100 % conversion was synthesized by RAFT using FDA and B12C4EMAAm monomers (85:15 wt/wt) in the presence of CTA and AIBN in TFT solvent as follows. B12C4EMAAm (1.5 g, 4.47 mmol), FDA (8.5 g, 16.4 mmol), CTA (0.26 g, 1.03 mmol), and

AIBN (0.079 g, 0.46 mmol) were weighed into a 100 mL round bottom flask (RB) with a rubber septum and dissolved in 12.5 mL TFT. The mixture was degassed with Ar gas and then heated to 65 °C with constant stirring. The monomer conversion was monitored by ¹H NMR by collecting the samples by stainless steel needle (Fig. S7). More AIBN (0.022 g, 0.14 mmol) was added to the reaction mixture after 48 h to boost the reaction. At the end of the reaction (70 h), the mixture was added dropwise in cold 200 mL pentane (0 °C) to precipitate the copolymer which was further washed twice with 100 mL pentane. The obtained orange solid mass was dried under vacuum (−1 bar) at 40 °C for 6 h.

The FDA to B12C4EMAAM ratio (mol/mol) in the copolymer and the molecular weight (M_n) of this copolymer were calculated from ¹H NMR spectrum in deuterated chloroform-1,1,2-trichloro-1,2,2-trifluoroethane (5:1 v/v) mixture (detailed calculation is reported in the Supporting Information, SI 2).

2.4. Characterization

The ¹H nuclear magnetic resonance (NMR) spectra (NMR) of monomers and copolymers were recorded at room temperature on a Bruker Avance 400 MHz spectrometer. The ¹H NMR spectra of the monomer were collected in deuterated chloroform, whereas a 1,1,2-trichloro-1,2,2-trifluoroethane-deuterated chloroform mixture (1:5 v/v) was used for the copolymer. The chemical shifts are in parts per million (ppm), where (s) means a singlet, (d) a doublet, (t) a triplet, (q) a quartet, and (m) a multiplet. Chemical shifts (¹H NMR) were referenced to the peak of residual CHCl₃ at $\delta = 7.26$ ppm.

Flash chromatography was performed in BUCHI Pure C-1815 Flash for the purification of B12C4EMAAM monomer.

Liquid chromatography mass spectrometry (LC-MS) analyses were performed on a MicroTof QII mass spectrometer from Bruker, coupled with an Ultimate 3000 liquid chromatography system from Thermo Fisher Scientific. The ionisation source was positive Electrospray Ionization.

FT-IR was performed using NICOLET, iS50 FT-IR for the characterization of the residues found in the extractor.

2.5. Cloud point measurement

Cloud-point measurements were carried out in a variable volume view cell thermostated with a double jacket and equipped with a sapphire window for visual observations [34]. The procedure is detailed in the Supporting Information, SI 3.

2.6. Transport experiments in scCO₂ and quantification

The salts (lithium salts and/or cobalt salt), ligand (B12C4) or macro-ligand p(B12C4EMAAM-*grad*-FDA) were placed in a 35 mL stainless steel extractor. List of solvents used for the dissolution of the salts, B12C4 and the copolymer is shown in Table S1. The quantities of the salts used in the blank experiments in the absence of crown ether are reported in the Supporting Information, Table S2. The quantities of salts and B12C4 used for the experiments are in Supporting Information, Table S3. The graphical image of our CO₂ setup is presented in the Supporting Information (Fig. S8). The closed extractor (outlet closed by a stop valve) was filled with CO₂ (where CO₂ acts as a solvent) at around 100 bar using a single piston pump (ISCO pump model 260D series) operating at $T = 35$ °C and $P = 270$ bar, and the magnetic stirring was set at 250 rpm. Then the desired temperature of the extractor ($T = 40$ °C) was adjusted *via* a heating jacket, and the pressure was adjusted at $P = 250$ bar by adding more CO₂. After reaching the desired pressure, the CO₂ supply was stopped, and the inlet to the extractor was closed using another stop valve. The experiment was performed under magnetic stirring at 700 rpm (batch process). After 3 h, the extractor was flushed with 140 mL CO₂ at a constant flow rate 5–8 mL/min at $P = 250$ bar and

$T = 40$ °C (conditions of ISCO pump: $T = 35$ °C and $P = 270$ bar, conditions of separator: $T = 25$ °C and $P = 50$ –60 bar) and then depressurized. Note that flushing the extractor with 220 mL CO₂ instead of 140 mL has no effect on the recovery yield. The constant flow of CO₂ is essential to maintain the constant pressure of the extractor to avoid the precipitation of the scCO₂ soluble material in the extractor and helps to transport the scCO₂ soluble material from the extractor to the separator. The samples collected at the end of the experiment are described in the Supporting Information, SI 4.

The amounts of Co and Li in the separator residue (S) and extractor residue (E) (Fig. S8) were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis. The metal left in the extractor (X, not extracted), the recovery yield of the metal isolated in the separator (Y), and the material balance (B, not measured) of the scCO₂ extraction for cobalt and lithium were calculated according to the following equations:

$$X_{Co} = \frac{m_{Co,E}}{\%m_{Co} \times m_{cobalt\ salt}} \times 100 \quad (1)$$

$$X_{Li} = \frac{m_{Li,E}}{\%m_{Li} \times m_{lithium\ salt}} \times 100 \quad (2)$$

$$Y_{Co} = \frac{m_{Co,S}}{\%m_{Co} \times m_{cobalt\ salt}} \times 100 \quad (3)$$

$$Y_{Li} = \frac{m_{Li,S}}{\%m_{Li} \times m_{lithium\ salt}} \times 100 \quad (4)$$

$$B_{Co} = \left[\frac{\%m_{Co} \times m_{cobalt\ salt} - m_{Co,S} - m_{Co,E}}{\%m_{Co} \times m_{cobalt\ salt}} \right] \times 100 \quad (5)$$

$$B_{Li} = \left[\frac{\%m_{Li} \times m_{lithium\ salt} - m_{Li,S} - m_{Li,E}}{\%m_{Li} \times m_{lithium\ salt}} \right] \times 100 \quad (6)$$

Where $m_{Co,S}$ and $m_{Li,S}$ are the mass of cobalt and lithium measured by ICP-OES in sample S. $m_{Co,E}$ and $m_{Li,E}$ are the mass of cobalt and lithium measured by ICP-OES in sample E.

$\%m_{Co}$ is the mass fraction of cobalt in cobalt salt, and $\%m_{Li}$ is the mass fraction of lithium in lithium salts.

$m_{cobalt\ salt}$ and $m_{lithium\ salt}$ are, respectively, the initial amount of cobalt salt and lithium salt introduced in the extractor.

3. Results and discussions

3.1. Use of benzo-12-crown-4-ether (B12C4) as a ligand for the transport of lithium and/or cobalt salts in scCO₂

3.1.1. Solubility of B12C4 in dense CO₂

The solubility of the crown ether B12C4 in dense CO₂ was determined by cloud point measurement. The solubility of B12C4 in scCO₂ is necessary to ensure a good contact between the metal salts and the crown ether to allow complexation in scCO₂. Fig. 1 shows the phase diagram of B12C4 in dense CO₂ at concentrations of 1.04 wt % and 3.03 wt % (B12C4/CO₂). The cloud point was determined as the point at which the medium turns cloudy from translucent (or *vice-versa*). The curve confirms that B12C4 is well soluble in dense CO₂ in the pressure range 70–220 bar and temperatures between 30 and 70 °C. Thus, under the experimental conditions of the extraction process (40 °C, 250 bar, [B12C4]=1.04 wt % and 3.03 wt % *versus* CO₂), B12C4 is fully soluble. The cloud point pressures of B12C4 were increased with increasing B12C4 concentration. In addition, an insoluble fraction (viscous liquid) was observed during the cloud point measurement when more concentrated B12C4 ([B12C4]=4.06 wt % *versus* CO₂) was used, indicating its limited use in scCO₂ (Fig. S9).

3.1.2. Transport experiments with B12C4 in scCO₂

For a neutral ionophore (B12C4), counter anions have a significant

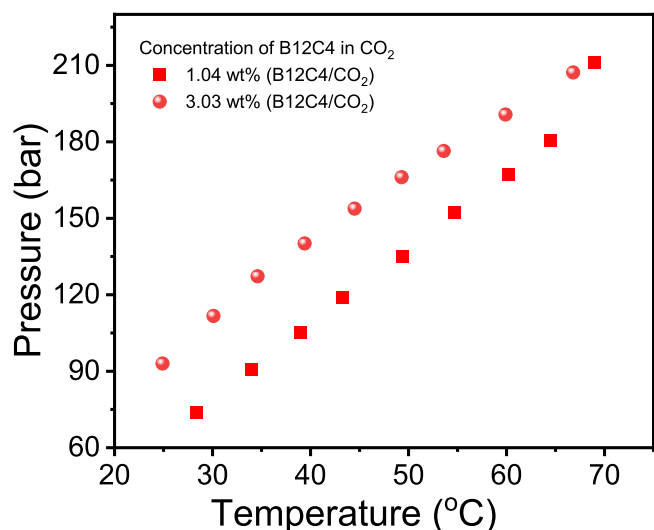


Fig. 1. Phase diagram of B12C4 in dense CO₂ at concentration 1.04 wt % and 3.03 wt % (B12C4/CO₂).

role in metal selectivity [35]. Therefore, to evaluate the effect of counter-anion on complexation, two lithium salts containing a monovalent anion (LiNO₃ and LiOAc) and two salts containing a divalent anion (Li₂SO₄ and Li₂CO₃) were used.

3.1.2.1. Behaviour of different lithium salts in scCO₂. Transport experiments were carried out with different lithium salts (LiNO₃, LiOAc, Li₂SO₄, and Li₂CO₃) in scCO₂ alone to check the solvation capability of scCO₂. The lithium recovery yields in the separator, determined by ICP-OES analysis using Eq. (4), are shown in Fig. 2A and Table S2.

When scCO₂ is used alone, the recovery yield of all the salts is below 4%. These results indicate that scCO₂ alone cannot solubilize these salts, and that only a small amount of them is carried away by scCO₂ during the rinsing step. Therefore, a CO₂-soluble complexing ligand is required to transport the metals from the extractor to the separator.

3.1.2.2. Transport of different lithium salts by B12C4 in scCO₂. The recovery yield of Li⁺ from LiNO₃ was increased to 17.3%, when scCO₂-soluble B12C4 was used (molar ratio B12C4:Li=5.6:1) as a complexing ligand in scCO₂ (concentration of B12C4 in CO₂ < 1 wt/wt versus CO₂) (Fig. 2B). For the other salts, i.e., LiOAc, Li₂SO₄ and Li₂CO₃, the addition of B12C4 did not improve the transport efficiency (Fig. 2B and Table S3, trials 2, 4, 5 and 6). In the case of LiNO₃, an additional CO₂-insoluble residue was recovered from the extractor together with LiNO₃. The FT-IR spectrum of this insoluble residue (Fig. 2C, red line) is similar to that of B12C4 (blue line). The characteristic band of B12C4 at 960 cm⁻¹ (C–O–C band), however, is red-shifted by 10–20 cm⁻¹, indicating the complexation of Li⁺ by B12C4 [36]. An additional band also appears at 835 cm⁻¹, related to the nitrate anion. Conversely, the FT-IR spectra of the extractor residues recovered when using LiOAc, Li₂SO₄ and Li₂CO₃ are identical to those of the pristine salts, indicating no complex formation (cf. Supporting Information, Fig. S10).

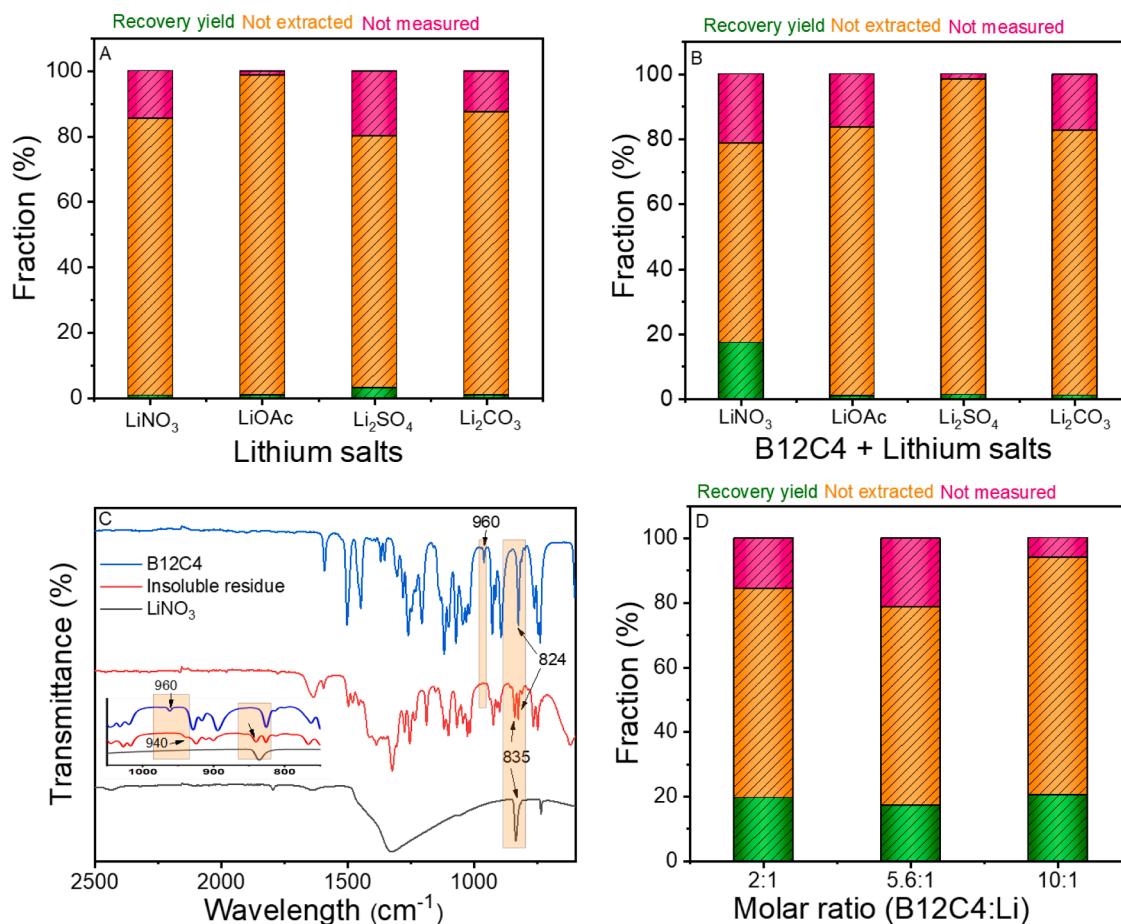


Fig. 2. (A): Bar diagram of recovery yield %, not extracted % and not measured % of lithium from LiNO₃, LiOAc, Li₂SO₄, and Li₂CO₃ salts in scCO₂ alone (experimental conditions: $T = 40\text{ }^{\circ}\text{C}$ and $P = 250\text{ bar}$), (B): Bar diagram of recovery yield %, not extracted % and not measured % of lithium from LiNO₃, LiOAc, Li₂SO₄ and Li₂CO₃ in the presence of B12C4 (molar ratio B12C4:Li=5.6:1), (C): FT-IR spectra of B12C4, insoluble residue and LiNO₃ and (D): Bar diagram of recovery yield %, not extracted % and not measured % of lithium from LiNO₃ by B12C4 in scCO₂ with different molar ratio of B12C4:Li (experimental condition $40\text{ }^{\circ}\text{C}$ and 250 bar).

Considering that the lithium recovery yield is significant only when using LiNO_3 , the effect of the molar ratio of B12C4 to metal ion was investigated only for this system. Interestingly, the recovery yield of lithium from LiNO_3 remained almost unchanged when the molar ratio was varied from B12C4:Li=2:1 (Li^+ recovery yield: 19.7 %) up to B12C4:Li=10:1 (Li^+ recovery yield: 20.6 %) (Fig. 2D and Table S3, trials 1, 2, and 3). A possible explanation is that the extraction is limited not by ligand availability but by other factors such as the solubility of the lithium nitrate-B12C4 complex in scCO_2 due to increasing polarity of the resulting complex, or limitations in phase transfer. These results suggest that optimizing the extraction process requires addressing the solubility limitations rather than increasing the B12C4:Li ratio alone. However, lithium nitrate is the only salt among those studied that facilitates the formation of a stable and partially CO_2 -soluble complex with benzo-12-crown-4 (B12C4) in scCO_2 .

The 17–20 % recovery yield of lithium from LiNO_3 may be related to the relatively soft nature of the nitrate anion or the low stability of LiNO_3 compared to other salts, according to Pearson's HSAB (Hard and Soft Acids and Bases) theory. Based on charge density and delocalization, the hardness order of the anions is: carbonate > sulfate > acetate > nitrate. CO_2 itself acts as a hard base [37], but above its critical pressure and temperature, it behaves as a soft solvent, thus leading to more favorable soft-soft interactions. The relative instability of sulfate, carbonate, and acetate anions in scCO_2 phase may hinder the complexation of their corresponding salts.

Moreover, the relative stability order of these salts is: $\text{Li}_2\text{SO}_4 > \text{Li}_2\text{CO}_3 > \text{LiOAc} > \text{LiNO}_3$ [38]. The lower stability of LiNO_3 might thus also favour lithium complexation by B12C4. Although the B12C4 has good solubility at 1 wt % in scCO_2 , the solubility of the [B12C4-Li] NO_3 complex in scCO_2 is limited, probably due to its higher polar nature.

3.1.2.3. Transport of cobalt salt by B12C4 in scCO_2 and selectivity comparison. Cobalt nitrate hexahydrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], bearing the same counter anion of LiNO_3 , was employed as the cobalt source in our experimental investigations to assess the selectivity of the crown ether towards cobalt. The recovery yield (%) of cobalt was determined by Eq. (3) (Fig. 3A).

When cobalt nitrate hexahydrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] was employed without the addition of a complexing ligand such as benzo-12-crown-4 (B12C4), only 10.6 % of cobalt was recovered in the separator, indicating its limited solubility in scCO_2 , confirming the results of Chirat *et al.* [15]. Surprisingly, the recovery yield was not improved even when B12C4 was added in a 10-fold molar excess relative to cobalt (recovery yield: 10.9 %) (Fig. 3A and Table S3, trials 7 and 8). In the presence of B12C4, a distinct pink residue was observed on the filter, in contrast to the original orange color of [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] (Fig. S11A). The FT-IR

spectrum of the pink residue (Fig. S11B, Supporting Information) differs significantly from that of pure [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], giving evidence of some interaction between the cobalt hydrated salt and the crown ether. Moreover, the pink color residue on the filter suggests that [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] is fully complexed by B12C4, and the recovery yield value indicates that the resulting complex is insoluble in scCO_2 .

In the case of a mixed system containing both LiNO_3 and [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] in the presence of B12C4 with a molar ratio B12C4:Li:Co=10:1:1, the recovery yields for cobalt and lithium were approximately 11 % and 15 %, respectively (see Fig. 3B and Table S3, trial 9). These findings further support the limited solubility of [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] in scCO_2 , as well as the insolubility of its complex with B12C4. Additionally, the 15 % recovery yield of lithium reinforces the observation that the [Li(B12C4)] NO_3 complex also exhibits limited solubility in scCO_2 .

3.2. Use of P(B12C4EMAAM-grad-FDA) copolymer as a macro-ligand for the transport of Li and/or Co salts in scCO_2

The above transport experiments showed that CO_2 -soluble B12C4 is not suitable for the transport of metal ions (Li^+ , Co^{2+}) because the formed polar complexes exhibit low solubilities in scCO_2 . Therefore, a more scCO_2 -soluble ligand is required to facilitate the transport of the polar complex from the extractor to the separator.

3.2.1. Synthesis of P(B12C4EMAAM-grad-FDA) copolymer

The P(B12C4EMAAM-grad-FDA) gradient copolymer was synthesized by RAFT polymerization using FDA as CO_2 -philic monomer units and B12C4EMAAM as complexing monomer units (Scheme 1). The orange colored copolymer was obtained with 50 % yield.

The ^1H NMR spectrum of the purified P(B12C4EMAAM-grad-FDA) copolymer is shown in Fig. 4 (^1H NMR of FDA monomer is in the Supporting Information, Fig. S5). The absence of signals at $\delta = 6.5$ and 5.5 ppm, with the exception of signal f, indicates that the sample contains no free monomer. The broad signal at $\delta = 6.2$ –5.9 ppm is due to the amido proton f of the B12C4EMAAM unit. The signal n of the chain transfer agent at $\delta = 4.43$ ppm merged with the methylene proton signal r of FDA at $\delta = 4.34$ ppm. δ values at 4.14, 3.82, and 3.77 ppm represent the methylene protons (i and i', j and j', k and l) of the crown ether of the B12C4EMAAM unit. The signal at 3.38 ppm represents the methylene proton (e, next to the amido nitrogen) of B12C4EMAAM unit. From the ^1H NMR spectrum, the FDA to B12C4EMAAM molar ratio was calculated to be FDA:B12C4EMAAM = 79:21 mol/mol in the copolymer (FDA/B12C4EMAAM=85/15 wt/wt), and the molecular weight (M_n) of this polymer was 15,560 g/mol calculated from ^1H NMR spectroscopy (cf. Supporting Information, SI 2, for detailed calculation).

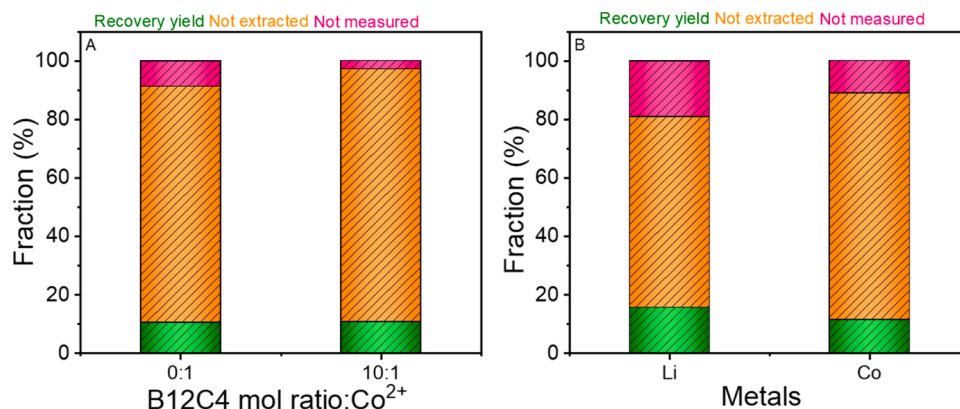
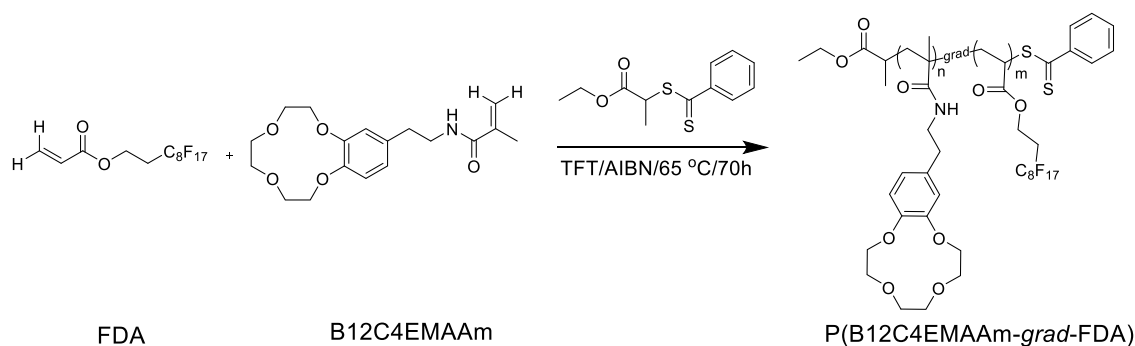


Fig. 3. (A): Bar diagram of recovery yield %, not extracted % and not measured % of cobalt from [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] in scCO_2 in the absence and the presence of B12C4 (molar ratio B12C4:Co=10:1) (experimental condition 40 °C and 250 bar), (B): Bar diagram of recovery yield %, not extracted % and not measured % of Li and Co by B12C4 in scCO_2 from a mixture of LiNO_3 and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, with molar ratio of B12C4:Li:Co = 10:1:1 (experimental condition 40 °C and 250 bar).



Scheme 1. Synthesis of P(B12C4EMAAM-grad-FDA) gradient copolymer.

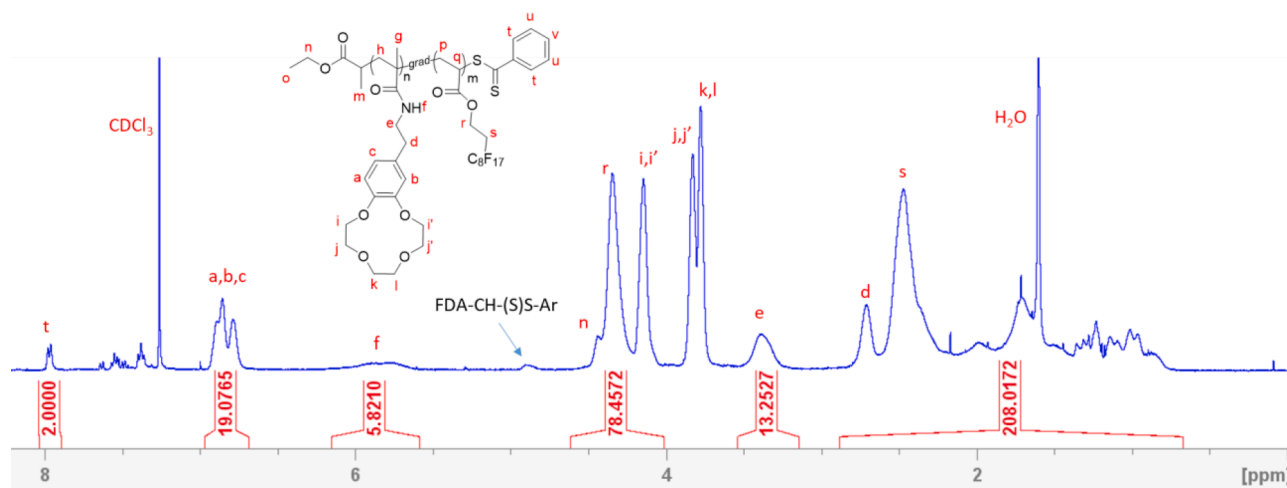


Fig. 4. ^1H NMR (400 MHz, rt) of P(B12C4EMAAM-grad-FDA) polymer in CDCl_3 -1,1,2-Trichloro-1,2,2-trifluoroethane (5:1 v/v) mixture.

3.2.2. Solubility of the copolymer in dense CO_2

Cloud point pressure measurements were used to evaluate the solubility of the gradient copolymer in scCO_2 at different copolymer concentrations (1 wt % and 3.4 wt %). The temperature–pressure phase diagram of the copolymer is presented in Fig. 5. The P(B12C4EMAAM-grad-FDA) copolymer is fully soluble in scCO_2 even at 3.4 wt %. In

contrast, B12C4 was only partially soluble in scCO_2 at such concentration (an insoluble fraction was observed for B12C4 at 4.06 wt % even above the cloud point). The cloud point pressures of P(B12C4EMAAM-grad-FDA) were compared with the cloud point pressures of PFDA homopolymer. The cloud point pressure of the copolymer is 30–60 bar higher than the cloud point pressure of PFDA homopolymer, illustrating the CO_2 -phobic character of the B12C4EMAAM monomer units in the copolymer. However, this P(B12C4EMAAM-grad-FDA) copolymer is still fully soluble in dense CO_2 . As a result, this copolymer can be used as a highly CO_2 -soluble macroligand in dense CO_2 .

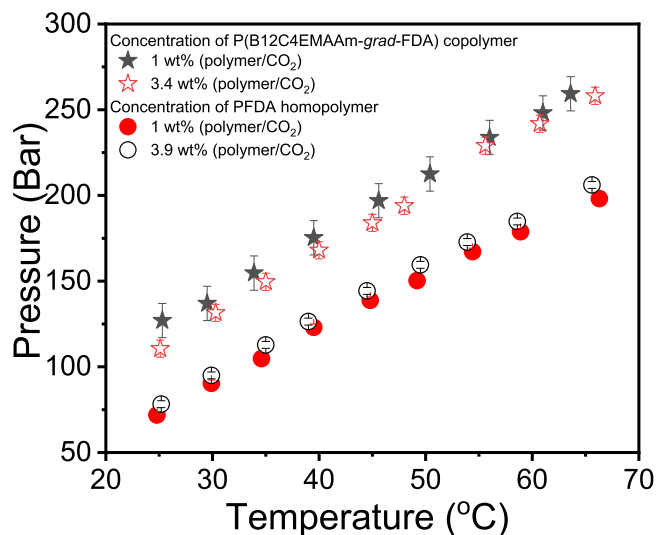


Fig. 5. Phase diagram of P(B12C4EMAAM-grad-FDA) copolymer (15 wt % B12C4EMAAM, $M_n=15,560$ g/mol) and PFDA homopolymer ($M_n=26,300$ g/mol) in dense CO_2 .

3.2.3. Transport experiments with P(B12C4EMAAM-grad-FDA) copolymer in scCO_2

Metal transport experiments with the gradient copolymer P(B12C4EMAAM-grad-FDA) were carried out following a procedure similar to that used for B12C4, using both LiNO_3 and $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ salts. Table 1 summarizes the experimental conditions, including the molar ratio of complexing groups to metal ions, the number of additives used, and other relevant parameters.

When the copolymer was used with a molar ratio B12C4EMAAM:Li=2:1 (Run 1), only pure LiNO_3 was observed in the extractor (no insoluble copolymer/metal complex nor copolymer was observed in the extractor), and the recovery yield of lithium in the separator was around 25 % (Fig. 6). Surprisingly, the same condition for cobalt (molar ratio B12C4EMAAM:Co=2:1) (Run 2) led to an even higher recovery yield of 89 % (Fig. 6). The increase of the recovery yield of both metals with the copolymer compared to the extraction with B12C4, and the absence of insoluble metal complex in the extractor are good signs of full solubility of the P(B12C4EMAAM-grad-FDA)/metal complex in scCO_2 .

Although lithium is expected to fit better in the B12C4 crown ether

Table 1

Quantities of the complexing group, additives, experimental conditions, and recovery yield of lithium and cobalt for the supercritical CO₂ extraction experiments ($P = 250$ bar, $T = 40$ °C).

Run	System	P(B12C4EMAAM-grad-FDA)		Mol ratio	H ₂ O (μL)	Recovery yield (%)	
		Mass of copolymer (mg)	Quantity of B12C4EMAAM unit (mol)			Li ⁺	Co ²⁺
1	LiNO ₃ (5.84 mg, 8.47×10^{-5} mol)	394.04	1.7×10^{-4}	B12C4EMAAM:Li = 2:1	0	25	–
2	[Co(NO ₃) ₂ ·6H ₂ O] (20.16 mg, 6.93×10^{-5} mol)	329.87	1.39×10^{-4}	B12C4EMAAM:Co = 2:1	0	–	89
3	LiNO ₃ (5.07 mg, 7.35×10^{-5} mol) + [Co (NO ₃) ₂ ·6H ₂ O] (21.8 mg, 7.52×10^{-5} mol)	144.47	7.72×10^{-5}	B12C4EMAAM:Li:Co = 1.05:1:1.02	0	41	56
4	LiNO ₃ (4.75 mg, 6.9×10^{-5} mol) + [Co(NO ₃) ₂ ·6H ₂ O] (20.4 mg, 7.02×10^{-5} mol)	582.78	2.5×10^{-4}	B12C4EMAAM:Li:Co = 3.6:1:1	0	46	84
5	LiNO ₃ (4.95 mg, 7.19×10^{-5} mol)	332.9	1.45×10^{-4}	B12C4EMAAM:Li = 2:1	10	83	–

cavity [39], [Co(NO₃)₂·6H₂O] can form several kinds of complexes with crown ethers. Co²⁺, having an ionic radius (79 pm) larger than the B12C4 cavity (radius), can form a pyramidal complex with one crown ether [40] and a sandwich complex [41] with two crown ethers of the B12C4EMAAM moiety (see Fig. 7A and B). It can also form a chain complex with B12C4EMAAM by forming hydrogen bonds between the H-atom of the water molecule present in the salt crystal and the oxygen atom of the crown (see Fig. 7C and D).

The presence of water molecules coordinating cobalt in [Co(NO₃)₂·6H₂O] might also influence the recovery yield of cobalt in the separator. The amount of water present in [Co(NO₃)₂·6H₂O] is almost 8 μL (in 7.5×10^{-5} mol salt), which is much less than the saturated amount of water in scCO₂ at $T = 40$ °C and $P = 250$ bar (118 μL). Indeed, the saturated amount of water in scCO₂ at 40 °C and 250 bar is 0.0093 mol fraction, as determined by Wang *et al.* [42]. Therefore, in this case, there

is not enough water for the formation of water-in-CO₂ microemulsion as described by Chirat *et al.* [15]. In this case, we assume that the water molecules complete the coordination sphere of Co²⁺ and, at the same time, form hydrogen bonds with B12C4EMAAM [43,44] (see Fig. 7C and D). In the case of lithium nitrate, on the other hand, the absence of water in the starting salt might explain the low recovery yield.

Interestingly, when a mixture of LiNO₃ and [Co(NO₃)₂·6H₂O] was used with a molar ratio B12C4EMAAM:Li:Co=1:1:1 (Run 3), the recovery yield of lithium was increased to 41 % and the recovery yield of cobalt was decreased to 56 % (Fig. 8A).

The low recovery yield (%) of cobalt in Run 3 compared to Run 2 is ascribed to the insufficient amount of complexing agent in the system per metal (deficit of complexing groups, 0.5 mol B12C4EMAAM for 1 mol of cobalt and 0.5 mol B12C4EMAAM for 1 mol of lithium). On the contrary, the recovery yield of lithium was increased from 25 % (Run 1) to 41 % (Run 3). We assume that some of the water molecules released from the hydrated cobalt salt [Co(NO₃)₂·6H₂O] may participate to the coordination of lithium, and form hydrogen bonds with B12C4EMAAM (see Fig. 8B), thus leading to an improved Li⁺ recovery yield compared to dry LiNO₃ (Run 1). Such a kind of hydrogen bonding was already reported by Bezdornikov *et al.* [36].

To improve the recovery yield, an excess of complexing agent was used (B12C4EMAAM:Li:Co=3.6:1:1) (Run 4). The recovery yield of cobalt was increased from 56 % (Run 3) to 84 % (Run 4). However, the recovery yield of lithium only slightly increased, from 41 % (Run 3) to 46 % (Run 4) (Fig. 9A). It is possible that the water molecules coming from the hydrated cobalt salt are not sufficient to further improve lithium recovery.

To strengthen this interpretation, the influence of water on the recovery of Li from LiNO₃ was studied by intentionally adding 10 μL of water to the mixture (Table 1, Run 5, the extraction procedure is described in Supporting Information SI 4). Indeed, such an addition impressively increases the recovery yield of lithium from 25 % (Run 1) to 83 % (Run 5) (Fig. 9B). Wai *et al.* and Lin *et al.* also used 10 μL of water in their experiments to increase the extraction efficiency of lanthanides, actinides, organic and inorganic mercury from solid materials, in addition to 5 mol % methanol modified CO₂ [45,46]. In that case, methanol increased the extraction efficiency by increasing the polarity of the fluid phase, while the addition of water provided an additional 11–18 % increase in extraction efficiency. The promoting effect of water has been

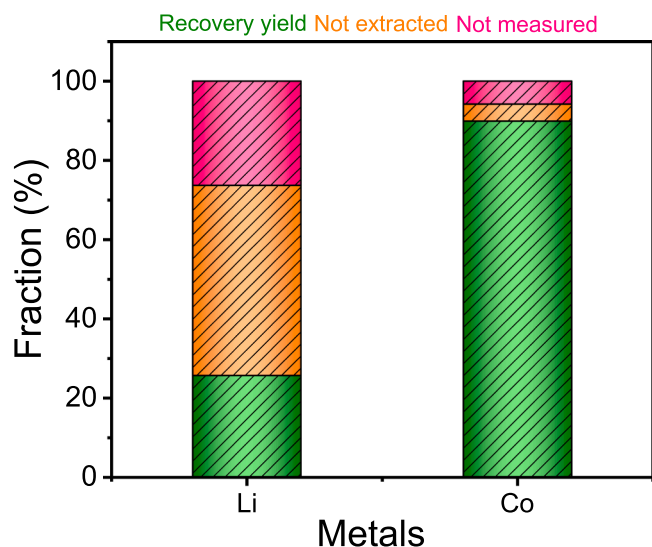


Fig. 6. Bar diagram of recovery yield %, not extracted % and not measured % of Li and Co by P(B12C4EMAAM-grad-FDA) copolymer in scCO₂ from LiNO₃ and Co(NO₃)₂·6H₂O, respectively, with individual molar ratio of B12C4:Li = 2:1 and B12C4:Co = 2:1 (experimental conditions: $T = 40$ °C and $P = 250$ bar).

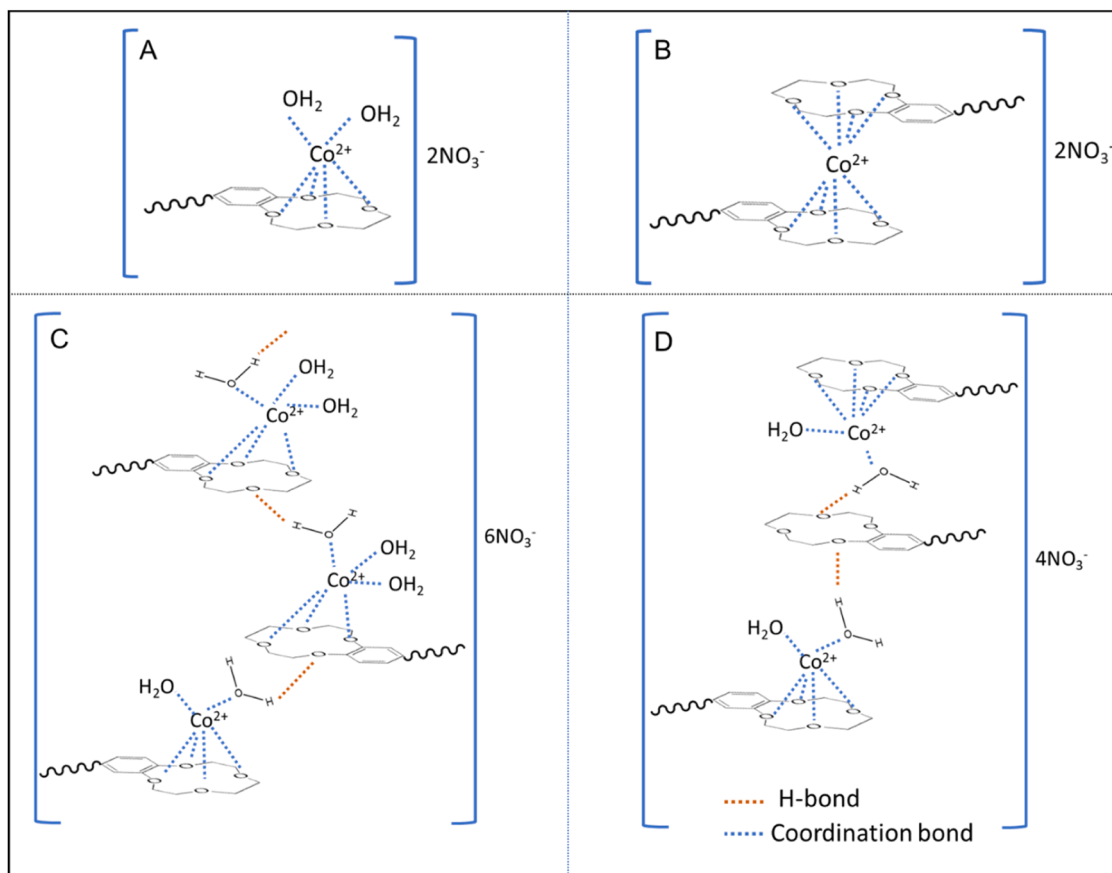


Fig. 7. Different kinds of complexation between $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ and $\text{P}(\text{B12C4EMAAm-grad-FDA})$ copolymer (A) pyramidal complex, (B) sandwich complex, and (C and D) complexation with hydrogen bonding.

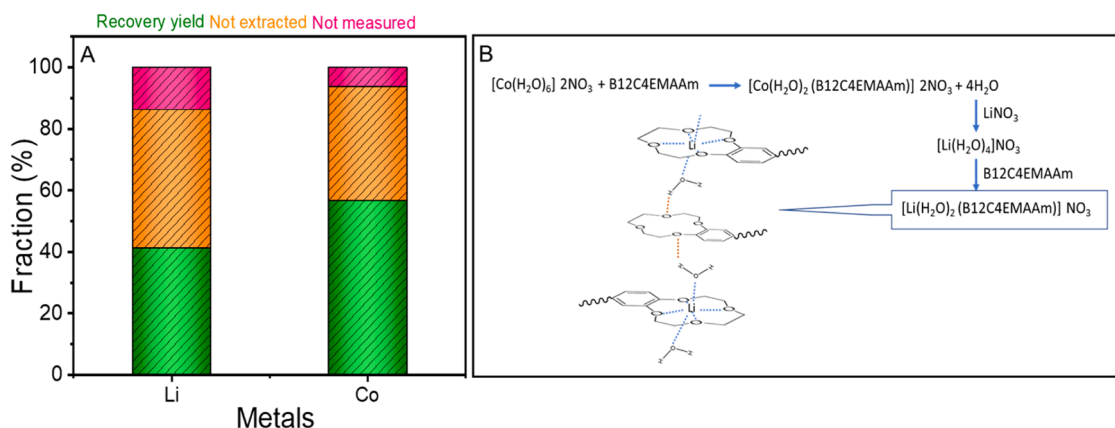


Fig. 8. (A) Bar diagram of recovery yield %, not extracted % and not measured % of Li and Co by $\text{P}(\text{B12C4EMAAm-grad-FDA})$ copolymer in scCO_2 from a mixture of LiNO_3 and $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, with molar ratio of $\text{B12C4EMAAm}:\text{Li}:\text{Co} = 1:1:1$ (experimental conditions: $T = 40^\circ\text{C}$ and $P = 250\text{ bar}$) and (B): Role of water molecules from the hydrated salt $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ in the complexing mechanism between LiNO_3 and $\text{P}(\text{B12C4EMAAm-grad-FDA})$.

attributed to its role in facilitating the release of metal complexes from the solid phase by forming a water adduct [like $\text{Ln}(2,2\text{-dimethyl-1-6,6,7,7,8,8,8\text{-heptafluoro-3,5-octanedione})\text{-H}_2\text{O}$] and enhancing their transfer into the supercritical phase. A comparable trend was also described by Chirat *et al.* [15], where the addition of 33 mg ($\approx 33\ \mu\text{L}$) of water improved cobalt extraction efficiency from 20 % to 66 %. Notably, in those studies, the water content exceeded its solubility limit in scCO_2 . In contrast, in the present work, the added water remains well below the solubility limit (Supporting Information SI 5). Therefore, the water molecules stabilize the LiNO_3 complex, possibly by participating in the

coordination of LiNO_3 and/or via hydrogen bond formation to the crown ether in scCO_2 [36]. The small amount of water used is not enough to enhance bulk solubility but instead plays a stabilizing role by complexation that contributes to the observed improvement in lithium recovery.

The copolymer $\text{P}(\text{B12C4EMAAm-grad-FDA})$ demonstrates a relatively high lithium recovery yield of approximately 83 % when water is present in the system, specifically at a molar ratio of $\text{H}_2\text{O}/\text{Li}^+ = 7.6$. Despite this promising recovery efficiency, the copolymer suffers from a drawback—namely, its poor selectivity between lithium ions (Li^+) and

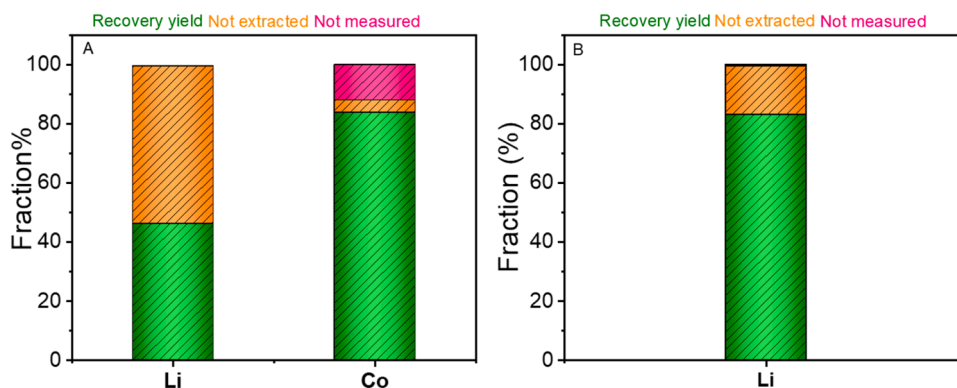


Fig. 9. (A): Bar diagram of recovery yield %, not extracted % and not measured % of Li and Co by P(B12C4EMAAm-grad-FDA) copolymer in $scCO_2$ from a mixture of $LiNO_3$ and $Co(NO_3)_2 \cdot 6H_2O$, with molar ratio of B12C4EMAAm:Li:Co= 3.6:1:1 (experimental conditions: $T = 40^\circ C$ and $P = 250$ bar) and (B): Bar diagram of recovery yield %, not extracted % and not measured % of Li by P(B12C4EMAAm-grad-FDA) copolymer in $scCO_2$ from $LiNO_3$ in presence of $10 \mu L H_2O$, respectively with molar ratio of B12C4EMAAm:Li= 2:1 (experimental conditions: $T = 40^\circ C$ and $P = 250$ bar).

cobalt ions (Co^{2+}). This lack of selectivity arises from the coordination chemistry of Co^{2+} with the B12C4 (benzo-12-crown-4) units incorporated in the copolymer. Owing to its slightly larger ionic radius (79 pm) relative to the intrinsic cavity size (radius) of B12C4 (50–65 pm), Co^{2+} can stabilize in the macrocyclic environment by adopting either an out-of-plane pyramidal complex or a sandwich-type complex (Fig. 7A and B). These interactions compromise the ability of the crown ether moiety to effectively discriminate in favor of lithium.

In contrast, molecules such as bipyridine are promising ligands for divalent metals, including Co^{2+} , Mn^{2+} , Ni^{2+} and Cu^{2+} [47]. Previous studies have exploited this property; for example, Yang *et al.* used bipyridine derivatives as chelating ligands for divalent metals (Co^{2+} , Ni^{2+} and Cu^{2+}) in $scCO_2$. Building on these insights, the addition of bipyridine with the P(B12C4EMAAm-grad-FDA) copolymer in the extraction system would present a compelling strategy to address its current limitations. Indeed, cobalt is expected to preferentially form

highly stable Co^{2+} -bipyridine complexes, which are generally insoluble in $scCO_2$. As a result, these complexes would precipitate in the extractor, thereby removing cobalt from the transport pathway. Consequently, the crown ether domains within the copolymer would be left with enhanced availability and selectivity for Li^+ transport. This would ultimately improve lithium selectivity by suppressing interference from competing multivalent cations, especially Co^{2+} , Ni^{2+} and Mn^{2+} , which are present in real cathode materials.

However, the applicability of P(B12C4EMAAm-grad-FDA) to real cathode materials is limited, because leaching and complexation must occur simultaneously in a single process. In the case of $LiCoO_2$, metal dissolution typically requires acidic protons to break the metal-oxygen bonds. However, under such acidic conditions, the complexation efficiency of crown ether units is significantly reduced due to the protonation of the ether oxygen atoms, diminishing their ability to coordinate with lithium [48].

Table 2

Comparison table of the amount of complexing ligand per metal, recovery yield of lithium and cobalt of our work and reported works in $scCO_2$.

Ligand	System	Amount of complexing ligand (CG) to metal	Li^+ Recovery yield (%)	Co^{2+} Recovery yield (%)	Ref
P(VBPDA-co-FDA)	Cobalt nitrate-contaminated lab coat	100 molar compared to cobalt	–	66	[15]
P(VBPDA-co-FDA)	$LiCoO_2$	4 molar compared to cobalt	60	60	[21]
TBP- HNO_3 adduct	NMC	5 mL/g (adduct/sample)	87	90	[17]
Bis(2-(2-butoxyethoxy)ethyl)-2,2'-bipyridine-4,4'-dicarboxylate+ perfluoro-1-octanesulfonic acid tetraethylammonium salt (PFOAT)	Ni, Mn, Fe, Cd, Pb, Zn, Co, and Cu from solid matrix	Bpy L:PFOAT: Metal= 10:50:1 (in mol)	–	48.3	[50]
Bis(2,2,3,3,4,4,5,5-octafluoropentyl) 2,2'-bipyridine-4,4'-dicarboxylate) + PFOAT	Mn^{2+} , Fe^{3+} , Cd^{2+} , Pb^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} from solid matrix	Bpy L:PFOAT: Metal= 50:50:1 (in mol)	–	69	[47]
Bis-trifluoroethylthiocarbamate (FDCC)	Cd, Co, Cu, Pb, Cr and Zn from solid samples	LiFDCC: total metals= 131:1	–	95	[51]
Fluorinated 14-crown-4 ether	Synthetic brine (10 mg/L lithium & 500 mg/L sodium, 40 mg/L magnesium)	50-fold excess compared to the lithium concentration	30	–	[27]
B12C4	$LiNO_3$	Molar ratio of CG: Li=2:1	15–20	–	Present work
P(B12C4EMAAm-grad-FDA)	$LiNO_3$	Molar ratio of CG: Li=2:1	25	–	Present work
P(B12C4EMAAm-grad-FDA)	$Co(NO_3)_2 \cdot 6H_2O$	Molar ratio of CG: Co=2:1	–	89	Present work
P(B12C4EMAAm-grad-FDA)	$LiNO_3$ & H_2O (10 μL)	Molar ratio of CG:Li=2:1	83	–	Present work
P(B12C4EMAAm-grad-FDA)	$LiNO_3$ & $Co(NO_3)_2 \cdot 6H_2O$	Molar ratio of CG:Li: Co=1:1:1	41	56	Present work
P(B12C4EMAAm-grad-FDA)	$LiNO_3$ & $Co(NO_3)_2 \cdot 6H_2O$	Molar ratio of CG:Li: Co=3.6:1:1	46	84	Present work

To overcome this limitation, a combined mechanoleaching–scCO₂ approach offers a promising alternative. Mechanochemical leaching of LiCoO₂ with either organic acid (citric acid) [49] or inorganic acid (HNO₃) produces mixed metal salts of lithium citrate or LiNO₃ and cobalt citrate or cobalt nitrate. Subsequent application of the scCO₂ extraction process to these salts could then enable selective separation of lithium from cobalt, overcoming the limitations of direct one-pot leaching–complexation with the copolymer.

Finally, the recovery yield and the number of complexing groups per metal are compared with other works in scCO₂ reported in the literature (Table 2). Wang *et al.* achieved only 48.3 % cobalt extraction efficiency using a non-fluorinated bipyridine derivative [bis(2-(2-butoxyethoxy)ethyl)-2,2'-bipyridine-4,4'-dicarboxylate] in combination with perfluoro-1-octanesulfonic acid tetraethylammonium salt (PFOAT) at a Bpy L:PFOAT: metal molar ratio of 10:50:1 [50]. Yang *et al.* later reported an improved 69 % cobalt extraction efficiency using a fluorinated bipyridine ligand [bis(2,2,3,3,4,4,5,5-octafluoropentyl)-2,2'-bipyridine-4,4'-dicarboxylate] with PFOAT at Bpy L:PFOAT: metal molar ratio of 50:50:1 from a mixed metal system containing Ni, Mn, Fe, Cd, Pb, Zn, Co, and Cu [47]. In another study, Wang *et al.* [51] achieved 95 % cobalt extraction efficiency, but using LiFDDC ligand at 131-fold molar excess relative to the target metal, highlighting significant cost and scalability limitations. Furthermore, Zhang *et al.* [17] reported non-selective extraction of 87 % lithium and 90 % cobalt using TBP–HNO₃ adducts in scCO₂, but these adducts are difficult to handle and pose safety concerns. Similarly, Vauloup *et al.* achieved 60 % lithium and cobalt recovery from LiCoO₂ using a P(VBPDA-co-FDA) copolymer, but only by applying a four fold molar excess relative to cobalt ions [21]. In contrast, in the present work, the P(B12C4EMAAm-grad-FDA) copolymer achieved 83 % lithium recovery and 89 % cobalt recovery using only 2 mol of ligand per mole of metal ions, which represents a clear advantage due to the substantially lower required ligand-to-metal ratio.

Although the lithium recovery is not yet selective, such non-optimized conditions demonstrate the efficiency of this approach by recovering lithium and cobalt using stoichiometric amounts of complexing groups.

4. Conclusion

Benzo-12-crown-4 ether was successfully employed to facilitate the transport of lithium and cobalt from lithium nitrate (LiNO₃) and cobalt nitrate hexahydrate [Co(NO₃)₂·6H₂O], respectively, in scCO₂. To improve the solubility of the metal complex and the extraction efficiency, a scCO₂-soluble gradient copolymer, P(B12C4EMAAm-grad-FDA), incorporating benzo-12-crown-4 moieties was synthesized for the selective complexation of Li⁺. Under supercritical conditions (*T* = 40 °C, *P* = 250 bar), the highly CO₂-soluble copolymer achieved recovery efficiencies of 83 % for lithium from LiNO₃ in the presence of small amounts of water and 89 % for cobalt from Co(NO₃)₂·6H₂O. A recovery of 46 % for lithium and 84 % for cobalt was obtained from a mixture of lithium nitrate (LiNO₃) and cobalt nitrate hexahydrate [Co(NO₃)₂·6H₂O], still requiring optimization of the water addition to reach quantitative extraction.

Undoubtedly, P(B12C4EMAAm-grad-FDA) proved to be an effective complexing ligand for both lithium and cobalt ions in scCO₂, especially in the presence of a small amount of water, well below the solubility limit in scCO₂. However, attaining selective coordination of lithium with respect to cobalt remains a significant challenge to achieve. Further improvements are needed to adapt the methodology to more complex cathode materials such as LiCoO₂, NMC or (thermal or mechanical) black mass, and to improve metal selectivity in competitive multi-element systems. Future work will focus on enhancing lithium selectivity and integrating scCO₂ extraction with *in situ* cathode leaching strategies. Furthermore, the P(B12C4EMAAm-grad-FDA) copolymer will also be tested for its ability to recover lithium from LIB electrolytes and,

ultimately, from black mass.

More generally, this study highlights the potential of a rational approach for the design of metal-complexing copolymer architecture to enable solvent-free recovery of critical metals, thereby advancing the circular economy in the context of battery recycling.

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CRediT authorship contribution statement

Rakhi Mondal: Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation. **Nicolas Stoffregen:** Methodology, Investigation. **Joshua Vauloup:** Writing – review & editing, Methodology, Data curation. **Cécile Bouilhac:** Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Data curation. **Nicolas Coppey:** Writing – review & editing. **Laure Monconduit:** Writing – review & editing. **Moulay T. Sougrati:** Writing – review & editing. **Lorenzo Stievano:** Writing – review & editing. **Patrick Lacroix-Desmazes:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization.

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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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.cej.2025.100883](https://doi.org/10.1016/j.cej.2025.100883).

Data availability

Data will be made available on request.

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