

Selective lithium separation from desalination concentrates via the synergy of extractant mixtures

E. Fernández-Escalante, R. Ibañez, Ma.-F. San-Román *

Departamento de Ingenierías Química y Biomolecular, ETSIIyT, Universidad de Cantabria, Avda. de los Castros, 46, Santander 39005, Cantabria, Spain

HIGHLIGHTS

- Selective separation of lithium from model seawater desalination brines
- 100 % Li⁺ extraction reached for FDOD•TOPO (pH = 9.0) from multicomponent model brines
- 95.4 % Li⁺ extraction reached for DBM•TOPO (pH = 12.2) from multicomponent model brines
- Not significant extraction of Na⁺, K⁺, Mg²⁺, Ca²⁺ and Sr²⁺ observed for FDOD•TOPO
- Not significant extraction of Na⁺, K⁺, Mg²⁺, Ca²⁺ and Sr²⁺ observed for DBM•TOPO

ARTICLE INFO

Keywords:

Lithium
SWRO brines
DBM•TOPO
FDOD•TOPO
Solvent extraction
Selectivity

ABSTRACT

Seawater reverse osmosis (SWRO) desalination plants generate high volumes of concentrates, which contain, in addition to major salts, some elements of growing interest in minor concentrations. This is the case of lithium, highly demanded in the battery industry. In this work, the separation of Li⁺ from model SWRO brines has been evaluated by obtaining Li⁺ extraction curves with the combination of extractants DBM•TOPO and FDOD•TOPO, proving that both mixtures are capable of extracting Li⁺ under basic pH conditions, due to the keto-enolic tautomerism of the β-diketones. Li⁺ extraction values of 95.4 % for DBM•TOPO (pH = 12.2) and 100 % for FDOD•TOPO (pH = 9.0) were achieved. This behaviour was verified by the FT-IR analysis of the sample before and after the Li⁺ extraction. Finally, the selective separation of Li⁺ against other cations, such as Na⁺, K⁺, Mg²⁺, Ca²⁺ and Sr²⁺, present in the model brines at higher concentrations, was determined. Under mentioned experimental conditions, these cations are not extracted, reaching to Li⁺ selective separation close to 100 %. This study shows the first results on the selective extraction of lithium in complex SWRO brines, fostered through promising extractants mixtures showing a synergic effect towards Li⁺ in such multicomponent matrices.

1. Introduction

Global population growth is leading to an increase in demand for resources. The depletion of conventional reserves encourages to explore alternative ways of producing freshwater, energy and raw materials. In recent years, an increasing number of desalination plants have been installed around the world in an effort to overcome freshwater scarcity [1]. In 2021, global desalination operating capacity was estimated at 79.35 million m³ day⁻¹ [2,3]. According to these studies, desalination capacity would almost double by 2050, based on past growth trends. With this high volume of desalination water, global brine production (concentrate from desalination plants) is estimated to be in the order of

141.5 million m³ day⁻¹ [4], and is expected to increase in the coming years, making this waste stream a new focus of exploration for its potential in mineral supply. Seawater contains practically all the elements of the periodic table, some of them valuable minerals, such as lithium, strontium or nickel, found in large quantities, taking to account the volume of seawater, but not in high concentrations. Knowing that these salts are concentrated in the brines from desalination plants, these waste streams can be converted into a new source of minerals [5,6]. The valorisation of seawater reverse osmosis (SWRO) desalination brines not only helps to recover different critical materials, but also reduces the impact generated by their discharge, being an advance in the sustainability of desalination processes, helping to promote the principles of the

* Corresponding author.

E-mail address: sanromm@unican.es (Ma.-F. San-Román).

<https://doi.org/10.1016/j.desal.2023.116525>

Received 23 December 2022; Received in revised form 24 February 2023; Accepted 25 February 2023

Available online 30 March 2023

0011-9164/© 2023 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

circular economy in this sector.

Among the variety of elements that can be recovered from brines, lithium is of crucial relevance due to its exponentially growing demand. Lithium production reached approximately 100,000 tons in 2021, 21 % more than in 2020, which suffered a drop due to the global COVID-19 pandemic impact on the economy, and almost doubled 2016 production [7,8]. This increase in production is linked to rising lithium consumption, reaching 93,000 tons in 2021, especially for lithium batteries which are widely used in the growing market for electric vehicles and portable electronic devices, and are increasingly used in power tools and grid storage applications. The global lithium resources were about 89 million tons (Mt) in 2021, highlighting the countries that conform to the lithium triangle: Bolivia (21.0 Mt), Argentina (19.0 Mt), and Chile (9.8 Mt). The amount of global Li^+ reserves from primary resources is approximately 22 Mt [8]. Several countries have significant quantities of this natural resource, but for some reasons (technical, economic or governmental) have not yet started to produce it. According to the EU, lithium overdoes the threshold for economic importance and it is very close to the threshold of the supply risk, hence it has been incorporated for the first time as one of the raw materials declared critical by the European Commission in 2020 [9], requiring the exploration and processing of all viable resources. Given that Li^+ is on the boundary between being economically feasible and economically challenging to recover from treated seawater brines [10], due to its low concentration in the brines and its market price, represents defiance to find new sources and recovery technologies that bring both economic and environmental improvements.

Thanks to the advances in the technology, the 4 most concentrated cations in seawater, sodium (Na^+ , 10,800 mg L^{-1}), magnesium (Mg^{2+} , 1290 mg L^{-1}), calcium (Ca^{2+} , 411 mg L^{-1}) and potassium (K^+ , 392 mg L^{-1}) are already commercially extracted [6,11,12]. Currently, the main challenge is to develop cost-effective strategies for the selective separation of minerals that have a high market value, but are found in low concentration in seawater and brines, such as lithium, which with an average concentration of 0.17 mg L^{-1} is the most abundant ion in the sea after the four currently commercially extracted [10]. Literature sources have reported that research into the separation of these minority salts has been undertaken with pure compounds [13–15]. Nevertheless, the study of the competition of the different ions present in these brines could be a novelty. According to literature, liquid-liquid (or solvent) extraction has been shown to be a widely used method for separating alkali cations [16–19], providing major benefits as the low cost, high product yield and recyclable extractants [5,17–20].

In previous works [21], we carried out a study via molecular simulation using *ab initio* Density Functional Theory aimed in order to select the most selective extractants towards lithium in the presence of Na^+ , K^+ , Mg^{2+} , Ca^{2+} and Sr^{2+} cations found in higher concentrations in the desalination brines. This study has represented an advance in knowledge, since at the time of writing, there were no experimental results in which all six cations were present at the same time; most of the literature does not consider, among others, Sr^{2+} cation. After a literature search, solvent extractants were selected, specifically from the family of organophosphates and β -diketones [21]. Organophosphates trioctylphosphine oxide (TOPO), tributyl phosphate (TBP), bis(2-ethylhexyl) phosphate (BIS) and tris(2-ethylhexyl) phosphate (TRIS) were chosen. From the β -diketones family, there is literature in which extractants as dibenzoylmethane (DBM), 2-thenoyltrifluoroacetone (TTA), benzoyltrifluoroacetone (BTA), heptafluoro-dimethyloctanedione (FDOD), and 4,4,4-trifluoro-1-(2-furyl)-1,3-butanedione (FTA), were used in combination with organophosphates as co-extractants to improve cation selectivity and extraction efficiency [22–24]. In the computational study, the equilibrium and thermodynamic properties of Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} and Sr^{2+} were obtained using Density Functional Theory (DFT). Based on the energetic results of the single systems, the organophosphate TOPO was selected to study the synergistic effect of β -diketone•organophosphate extractants on Li^+

extraction. The combination of β -diketones with TOPO in a 1:1 ratio provided better values of free energy compared to the simple systems. Finally, the selective extraction of lithium in the presence of the other cations was predicted by the analysis of the relationship between the equilibrium constants of complexation and hydration reactions. The FDOD•TOPO system with respect to the group II cations (Mg^{2+} , Ca^{2+} and Sr^{2+}), and the DBM•TOPO system with respect to the group I cations (Na^+ and K^+) were the most selective mixtures [21]. These results have provided knowledge on the behaviour of the most promising extractants towards Li^+ in seawater desalination concentrates, thus demonstrating the importance of molecular simulation for forecasting scenarios, reducing the experimental work required in these studies.

Facing advancing knowledge, the aim of this work is to determine the feasibility at laboratory scale of the selective and effective extraction of Li^+ in the presence of other competitive ions found in SWRO, employing extractant mixtures and liquid-liquid extraction as the separation technology. For this purpose, organophosphate TOPO, and β -diketones DBM and FDOD have been used as extractants. The extraction of the cations has been studied with the extractants individually and with organophosphate• β -diketone systems, in order to evaluate the synergistic effect between them during the extraction process. Extraction performances of Li^+ and other cations have been obtained for each combination of extractants. The results obtained are expected to provide a preliminary view of the behaviour of the most promising extractants towards Li^+ from seawater desalination concentrates.

2. Materials and methods

2.1. Materials and instruments

All used reagents were of analytical grade and were dissolved in deionized water purified. Lithium chloride (LiCl , >99 %) was purchased from Labkem (Spain). Sodium chloride (NaCl , >99.5 %), calcium chloride (CaCl_2 , 99 %), and strontium chloride (SrCl_2 , >99 %), were purchased from Fisher Scientific (Belgium). Potassium chloride (KCl , >99.5 %) was purchased from Scharlab S.L. (Spain). Magnesium chloride 6-hydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), and ammonia (NH_3 , 25 %) were obtained from PanReac AppliChem (Spain). Nitric acid (HNO_3 , 65 %) was purchased from Sigma Aldrich (Germany). Standard solutions of 1000 mg L^{-1} each of lithium, sodium, potassium, magnesium, calcium and strontium were obtained from Agilent (CA, USA). Deionized water was produced by a Milli-Q ultrapure water purification system (Millipore). Extractants dibenzoylmethane (DBM, 98 %), and trioctylphosphine oxide (TOPO, 99 %) were obtained from Acros Organics (China and Japan respectively). Extractant heptafluoro-dimethyloctanedione (FDOD, 95 %) was purchased from AA Blocks (CA, USA). Kerosene (ShellSol D70) was purchased from Kremer (Germany).

The instruments used were as follows: a pH meter (GLP 22, CRISON) to measure the pH of the aqueous phase. A thermostatically heated magnetic stirrer (2mag) was used for the liquid-liquid extraction process. A Microwave Plasma-Atomic Emission Spectroscopy (MP-AES 4210, Agilent Technologies) was used to determine the concentration of cations in the aqueous solution before and after extraction. Finally, a Fourier transform infrared (FT-IR) spectrophotometer (Spectrum 65, Perkin Elmer) was used to analyse the structure of individual extractants and the composition of mixtures.

2.2. Experimental procedure

In order to prepare the aqueous phases, the required amounts of LiCl , NaCl , KCl , MgCl_2 , CaCl_2 and SrCl_2 were dissolved in ultrapure water. A specific volume of NH_3 or HNO_3 was added when specific pH was required. Table 1 shows range of concentration of the main cations present in SWRO brines according to the literature. Additionally, cation concentrations used in the multicomponent aqueous phases (Sections 3.3.2 and 3.3.3) are shown in Table 1. The initial conditions used in

Table 1

Range of concentration of the main cations present in SWRO brines according to literature. Composition of model brine used in this work.

Concentration range in brines						
Li ⁺	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Sr ²⁺	
0.3–2	1670–25,000	43.1–1094	200–7600	87–2800	4.56–121	Real brines (mg L ⁻¹) [25–27]
2	2000	990	1673	1090	121	Model brines (mg L ⁻¹) This work

individual cation aqueous phase have been specified within each of these parts (Sections 3.1 and 3.3.1).

In the same way, two different kinds of organic phases have been used: i) single extractant (organophosphate or β -diketone) and ii) binary mixtures (organophosphate + β -diketone). The organic phase with only one extractant was prepared by diluting in kerosene TOPO or β -diketone (DBM or FDOD). Then heated and stirred at 70 °C on the stirrer to obtain a clear liquid, and subsequently cooled to room temperature. The organic phase compose TOPO and DBM or FDOD was mixed and diluted in kerosene in 1:1 molar ratio, selected according to the previous results obtained by molecular simulation. Combining the β -diketones with TOPO in a 1:1 ratio the reaction was spontaneous ($\Delta G < 0$) while a 1:2 ratio implicated a nonspontaneous reaction ($\Delta G > 0$). This scenario can be due to steric issues, as the interaction of the TOPO chains with the β -diketone radicals could hinder -or at least compete with- the coordination of the phosphate's oxygen atoms around the cations [21].

Organic and aqueous phases were mixed in glass bottles with equal volume ratio (O/A = 1) and were shaken vigorously in the stirrer at a speed of 500 rpm until the extraction equilibrium was achieved. All experiments were carried out at room temperature. Later, the salt content of the aqueous phase was analysed by the MP-AES. Previously, it was diluted with ultrapure water and acidified with 5 % HNO₃. The cation extraction was defined as Eq. (1):

$$\text{Extraction (\%)} = \frac{C_0 - C_e}{C_0} 100 \quad (1)$$

where C_0 is the initial concentration of the cation in the aqueous phase (mg L⁻¹), and C_e is the equilibrium concentration of the cation in the aqueous phase (mg L⁻¹).

3. Results and discussion

3.1. Feasibility of cations extraction from individual cations aqueous phase using β -diketone or/and organophosphate

The feasibility of β -diketone or/and organophosphate as an organic phase was evaluated by extraction experiments performed using individual cations aqueous phase. In this way, six individual aqueous phases were prepared, one for each cation, Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺ and Sr²⁺, with an initial concentration of 0.03 mol L⁻¹. The ratio [Extractant]/[Cation] = 2 was chosen based on the literature. Thus, Zhang et al. [13] achieved 80 % Li⁺ extraction using HFTA•TOPO with a molar ratio to Li⁺ between 2 and 3. Kinugasa et al. [28] applied the β -diketone•organophosphate mixture of LIX 54•TOPO for lithium extraction, testing with molar ratios between 1 and 5. Pranolo et al. [29] employed LIX 54 with the neutral ligand Cyanex 923 with a molar ratio [Extractant]/[Li⁺] = 4, reaching 95 % extraction. In another study, Zhang et al. [30] used a HBTA•TOPO mixture with a molar ratio to Li⁺ of 3, achieving approximately 80 % of extraction. The concentration of TOPO, DBM and FDOD was 0.06 mol L⁻¹ when used individually and 0.03 mol L⁻¹ for each extractant when used in combination. Extraction experiments were performed at a neutral initial pH of the aqueous phase $\text{pH}_{\text{aq},i} \approx 6.0$, below the pK_a of each extractant (8.95 for DBM and 6.71 for FDOD [31]). Using DBM, FDOD and TOPO individually neither Li⁺ nor Mg²⁺ were extracted. Na⁺ and K⁺ extractions did not exceed 2 %. Ca²⁺ and Sr²⁺ presented the highest extraction values, but did not exceed 10 %. Using β -diketone•TOPO combinations, Sr²⁺ was the cation with the highest extraction value (below 10 %), while the rest of the cations were extracted between 1 and 5 %.

Literature sources reported the extraction of lithium from the aqueous phase using an extraction system consisting of β -diketone and organophosphate at basic pH. In these conditions, the β -diketone is protonated and as a consequence, a proton-cation exchange with the extractants is

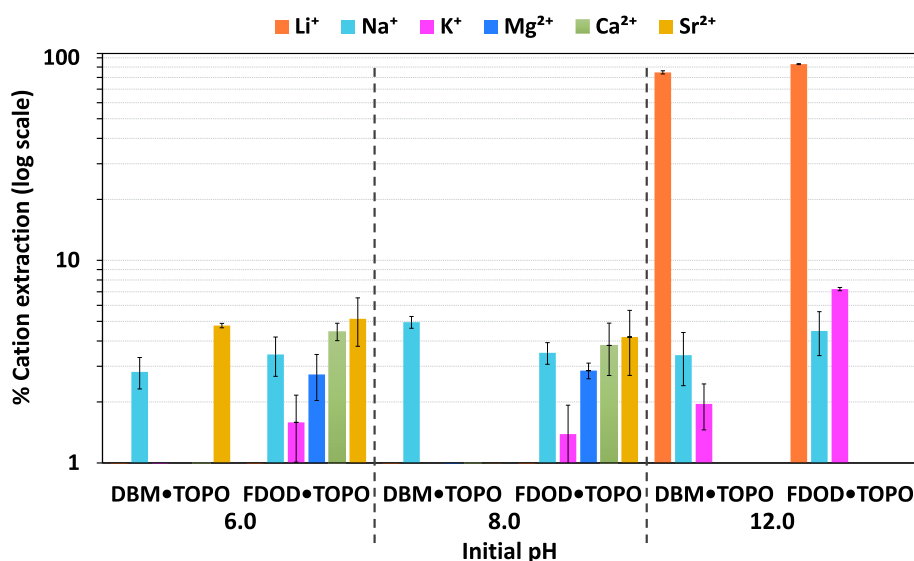


Fig. 1. % Extraction of Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺ and Sr²⁺ from individual cations aqueous phase at different $\text{pH}_{\text{aq},i}$ values (6.0, 8.0 and 12.0) using the mixtures extractants DBM•TOPO and FDOD•TOPO.

produced [32,33]. Accordingly, experiments using an aqueous phase with individual cations and individual extractants and mixtures β -diketone•organophosphate ($[\text{Extractant}]/[\text{Cation}] = 2$) were carried out at the $\text{pH}_{\text{aq},i}$ to 8.0 and 12.0. Group II cations (Mg^{2+} , Ca^{2+} and Sr^{2+}), which tend to precipitate as salts at basic pH values, were not evaluated at $\text{pH} > 9.0$ [25,34–36]. The obtained results were similar to those obtained at $\text{pH}_{\text{aq},i} \approx 6.0$, for both the individual and mixtures extractants.

In order to better determine the influence of extractants synergic effect at different pHs, extraction experiments were carried out using a concentration of 0.02 mol L^{-1} of each cation and mixtures of 0.1 mol L^{-1} β -diketone plus 0.1 mol L^{-1} TOPO. Thus, the ratio $[\text{Extractant}]/[\text{Cation}]$ was increased to 10, employing an excess of organic phase to encourage the extraction. The results obtained are reflected in Fig. 1. It can be observed that at a $\text{pH}_{\text{aq},i} \approx 8.0$, above the pK_a value of FDOD (6.7), extraction of all cations is lower than 10%. In contrast, in the case of an extremely basic $\text{pH}_{\text{aq},i} = 12.0$, the DBM•TOPO mixture was able to extract about 85% of Li^+ , while FDOD•TOPO extracted 93%. At this pH, extraction of magnesium, calcium and strontium was not carried out due to the precipitation phenomenon.

3.2. Analysis of extraction mechanism of systems Li^+ • β -diketone•organophosphate

Given the promising results obtained in the feasibility study, the FT-IR spectra were performed on the organic phases DBM•TOPO and FDOD•TOPO, in order to know the pH influence on the Li^+ extraction process. The FT-IR spectra of the individual extractants are included in the Supplementary data. FT-IR analysis was performed for both mixtures and three experimental conditions: 1) before extraction, when the organic phase has not been contacted with the aqueous phase, 2) after Li^+ extraction from the aqueous phase at acidic initial pH, $\text{pH}_{\text{aq},i} = 3.0$, and 3) after Li^+ extraction from the aqueous phase at basic initial pH, $\text{pH}_{\text{aq},i} = 12.0$. Fig. 2 shows the FT-IR analysis for the DBM•TOPO combination. As can be observed, before and after Li^+ extraction from the acid aqueous phase, no change in the spectrum was observed, namely, the structure of the extractants was not modified. The characteristic peak at 1220 cm^{-1} belongs to the $\text{P}=\text{O}$ stretching vibration of TOPO, which remained unchanged before and after extraction in both pH conditions. This fact is indicative of a purely electrostatic attraction between the cation and the extractant, with hardly any charge transfer to the cation, according to the results of the molecular simulation study

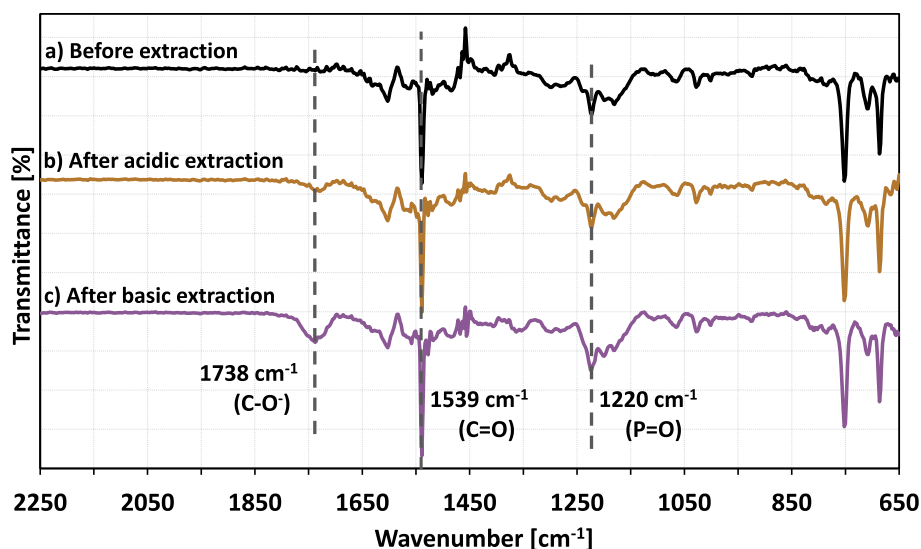


Fig. 2. FT-IR spectra of organic phase DBM•TOPO a) before Li^+ extraction, b) after Li^+ extraction in acidic $\text{pH}_{\text{aq},i}$, and c) after Li^+ extraction in basic $\text{pH}_{\text{aq},i}$.

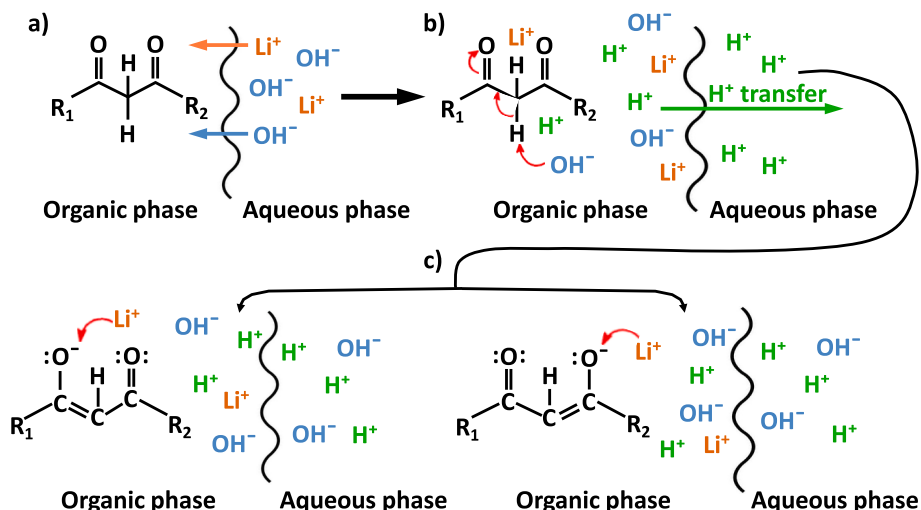


Fig. 3. Tautomeric effect of a β -diketone at basic medium in presence of Li^+ .

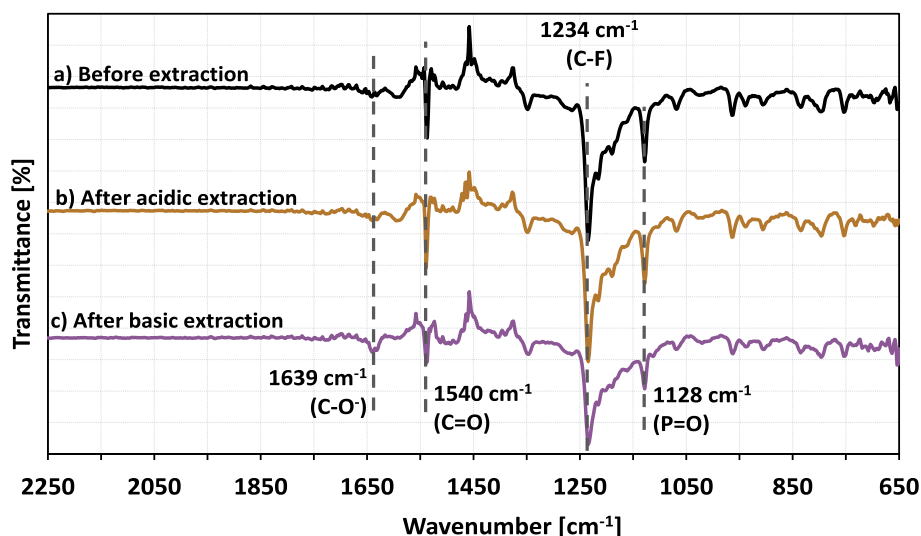


Fig. 4. FT-IR spectra of organic phase FDOD•TOPO a) before Li^+ extraction, b) after Li^+ extraction in acidic $\text{pH}_{\text{aq},i}$, and c) after Li^+ extraction in basic $\text{pH}_{\text{aq},i}$.

from Coterillo et al. [21]. The peak at 1539 cm^{-1} was assigned to the C=O stretching vibration of DBM, which exhibited a higher intensity after the extraction in a basic medium (Fig. 2c). Finally, a new band formed in the spectrum of extraction, 1738 cm^{-1} , at basic pH. This peak is characteristic of an enol group corresponding to the family of 1,3-diketone, after suffering the tautomeric effect [37], i.e., Fig. 2c shows the spectrum corresponding to the behaviour of the keto-enol equilibrium or keto-enol tautomerism. In general, α -hydrogens directly adjacent to a carbonyl group, display unusual acidity. Because of this acidity, many carbonyl groups containing molecules undergo a proton-transfer equilibrium called keto-enol tautomerism. The keto form implies that the tautomer contains a (or various) carbonyl bond while enol implies the presence of a double bond and a hydroxyl group. In neutral medium, tautomerisation is slow but it can be accelerated by catalysis with acids or bases. As shown in Fig. 3, in basic medium, in a first step, anion hydroxyl is transferred to the organic phase attacking the acid carbon of the extractant and stripping off an α -hydrogen to form an alkene with the adjacent carbon. This causes the π electrons of the carbonyl to move onto the oxygen forming an enolate anion. In Li^+ presence, the oxygen of the enolate anion bond with said cation, so that the proton is transferred to the aqueous phase in order to maintain the electroneutrality of the charges in both phases (Fig. 3c) [22,30,35,38,39].

Similarly, Fig. 4 shows the FT-IR analysis for the FDOD•TOPO combination. Before extraction and after extraction from an acid system ($\text{pH}_{\text{aq},i} = 2.0$), the spectra were practically the same, confirming that no Li^+ has been extracted, and therefore the structure of the extractants had not changed. The characteristic peak at 1128 cm^{-1} corresponds to the stretching vibration P=O of TOPO. This peak has varied with respect to FT-IR of the DBM•TOPO system due to FDOD having a very electronegative radical, F^- , in a close wavelength, 1234 cm^{-1} belonging to the C-F. At basic system ($\text{pH}_{\text{aq},i} = 11.0$), a new peak was observed at 1639 cm^{-1} , in line with the fact that at higher wavenumbers the band of the keto form and the unbound enolic form of the β -diketone appear. These results confirmed Li^+ •FDOD•TOPO complex was formed.

3.3. Extraction Li^+ /competitive cations from model brine solutions using β -diketone•organophosphate systems

3.3.1. Separation system definition

As conclusion of the experimental results obtained in the sections previous, in a second stage, the study of the extractants concentration influence on the separation of lithium from model brines solutions was carried out. For this purpose, higher molar ratios [Extractant]/ $[\text{Li}^+]$ have been used in order to promote the extraction process. All operation

conditions are indicated in Table 2. The experimental results obtained are shown in Fig. 5.

Fig. 5 shows that, under the experimental conditions used, it is possible to extract $>90\%$ of Li^+ with both systems, reaching 100% in the case of FDOD•TOPO system for $[\text{FDOD}\cdot\text{TOPO}]/[\text{Li}^+]$ higher than 50. On the other hand, $[\text{DBM}\cdot\text{TOPO}]/[\text{Li}^+]$ molar ratios below 25 are not able to significantly extract Li^+ from the feed solution while requiring a ratio of 175 to achieve 90% extraction. From these results,

Table 2
Operating conditions for the selection of the extractant concentration.

Set conditions						
Initial pH in the aqueous phase ($\text{pH}_{\text{aq},i}$)	12					
Volumetric ratio organic/aqueous phase (O/A)	1					
Molar ratio β -diketone/TOPO	1					
Li^+ concentration in the aqueous phase ($[\text{Li}^+]$)	2 mg L^{-1} ($2.88\cdot 10^{-4}\text{ mol L}^{-1}$)					
Variable conditions						
Extractants/ Li^+ concentration ratio	15	25	50	100	150	200
Extractants concentration [mol L^{-1}]	0.004	0.007	0.014	0.029	0.043	0.058
Operation time (min)	10^a					

^a Equilibrium reach at 10 min in all experiments.

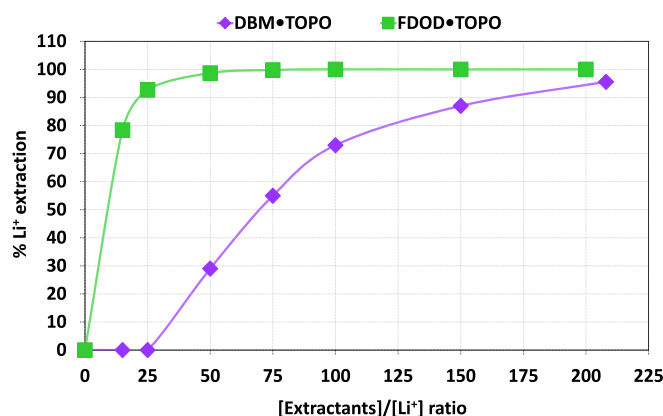


Fig. 5. Li^+ extraction percentage for molar ratios $[\text{DBM}\cdot\text{TOPO}]/[\text{Li}^+]$ and $[\text{FDOD}\cdot\text{TOPO}]/[\text{Li}^+]$ showed in Table 2.

$[\text{FDOD}\bullet\text{TOPO}]/[\text{Li}^+] = 50$ and $[\text{DBM}\bullet\text{TOPO}]/[\text{Li}^+] = 200$ molar ratios were chosen, in order to study experimental extraction for each individual cation and into their mixtures. The results of these experiments are presented and discussed in the following sections.

3.3.2. Cation extraction curves for DBM•TOPO system

The defined separation system was used to study the extraction and possible competitiveness of the alkaline and alkaline earth cations present in the seawater desalination concentrates versus Li^+ . The extraction curves for the cations Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} and Sr^{2+} , with the concentrations corresponding to the model brines of this work (indicated in Table 1), were carried out for DBM•TOPO combination. In the first stage, the extraction curves for all the cations were carried out individually, i.e., with monocomponent aqueous phases. Fig. 6a shows the extraction percentages of each cation for the DBM•TOPO extractants combination against equilibrium pH. Mg^{2+} , Ca^{2+} and Sr^{2+} were not assessed beyond the initial $\text{pH}_{\text{aq},i}$ in the aqueous phase of 9.8, 11.15 and 11.33, respectively, because they precipitate in hydroxides and carbonates form [40]. Fig. 6b shows the possible bonding mechanism of $\text{Li}^+\bullet\text{DBM}\bullet\text{TOPO}$ and Fig. 6c shows the variation of the equilibrium pH of the aqueous phase with respect its initial pH.

Fig. 6a shows that alkaline cations, Na^+ and K^+ , and alkaline earths, Ca^{2+} , Mg^{2+} and Sr^{2+} , were not extracted at any pH evaluated. The Li^+ behaviour was completely different. As can be observed in Fig. 6a, lithium began to be extracted, $\approx 4\%$, at an equilibrium pH of around 8.5,

increasing exponentially until 95.4% at an equilibrium pH = 12.2. This phenomenon is related to the tautomeric effect of β -diketone DBM, that relies on the aqueous phase initial pH and extractant pKa. When $\text{pH} \approx \text{pKa}$, i.e., in presence of hydroxyl ions, DBM undergoes an enolization process, as has been described in Section 3.2 (Fig. 3). Li^+ , due to its small size has a coordination number = 4 and hybridation sp^3 , i.e., four empty orbitals capable to coordinate with four oxygen atoms, corresponding to i) oxyanion of the DBM extractant, which is exchanged for the proton from the acid carbon, ii) ketone group of DBM extractant, iii) oxygen atom of the TOPO extractant, and possibly, iv) oxygen atom of a one water molecule, that carries with Li^+ from the aqueous phase, to form a chelate ring [39,41–43] (Fig. 6b). As can be seen in Fig. 6c, when the aqueous phase is acidic, the protons are transferred to the organic phase, producing the enolic form of the extractant molecule (Fig. 6c, 1), however, this reaction hardly occurs, since it is hugely unfavorable, therefore hardly influences the equilibrium pH. As soon as the initial pH of the aqueous phase increases to around the pKa value of the extractant, the migration of hydroxyl ions from the aqueous phase to the organic phase takes place together with the transfer of α -hydrogens from the DBM extractant to the aqueous phase, taking place to the enol and keto forms of the β -ketone, which coexist in equilibrium (Fig. 6c, 2). In this case, it produces a decrease in the equilibrium pH of the aqueous phase, with respect to the initial pH. If the aqueous phase has a fairly basic initial pH, the enolate form of the organic molecule is produced, which facilitates its binding to the Li^+ cation, leading to extraction (Fig. 6c, 3). In this

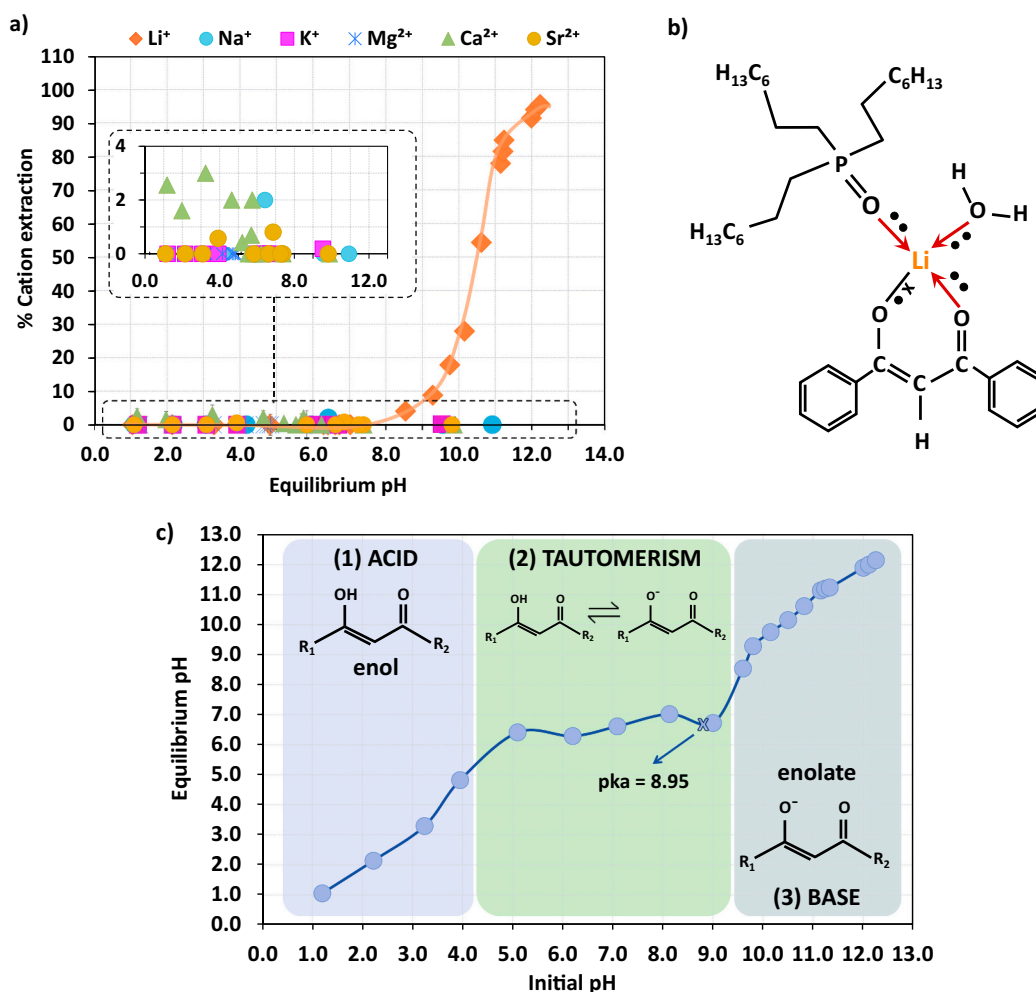


Fig. 6. a) Extraction percentage of the cations from monocomponent systems versus equilibrium pH, b) possible bonding mechanism of $\text{Li}^+\bullet\text{DBM}\bullet\text{TOPO}$, c) variation of the equilibrium pH versus the initial pH of the aqueous phase. $[\text{DBM}] = 0.03 \text{ mol L}^{-1}$; $[\text{TOPO}] = 0.03 \text{ mol L}^{-1}$; O/A = 1; time of extraction = 10 min.

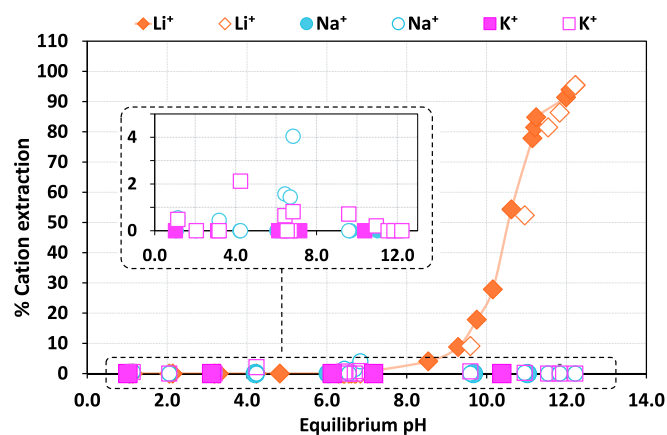


Fig. 7. Extraction percentage of the cations from monocomponent systems (filled) and multicomponent systems (empty). DBM•TOPO. [DBM] = 0.03 mol L⁻¹; [TOPO] = 0.03 mol L⁻¹; O/A = 1; time of extraction = 10 min.

situation, initial pH is similar equilibrium pH (Fig. 3). As described, the combination of DBM•TOPO extractants is not able to extract any of the alkali cations K⁺ and Na⁺ at any pH value. This singularity is directly related to the ionic radius and to the coordination number of Li⁺ versus Na⁺ and K⁺. The ionic radius of lithium, 0.68 Å, is very small compared

to the ionic radius of Na⁺, 0.97 Å, and K⁺, 1.33 Å. This results in a higher value of charge density (z/r) for lithium, 1.47 Å⁻¹, compared to Na⁺, 1.03 Å⁻¹, and K⁺, 0.75 Å⁻¹. As a consequence, the combination with the extractants becomes weaker for Na⁺ and K⁺, nevertheless, for Li⁺, leads to stronger electrostatic interactions and to the formation of a more stable complex. Besides, it is well-known that Na⁺ and K⁺ form complexes with β -diketones employing a coordination number of 6. So that is probably, that the generated bonds in these types of complexes are very weak, among other reasons, because it requires the incorporation of two water molecules in order to obtain hexa-coordination, i.e., an octahedral geometry.

The influence of Na⁺ and K⁺, Ca²⁺, Mg²⁺ and Sr²⁺ in the extraction of Li⁺ by means DBM•TOPO system was experimentally evaluated. Fig. 7 shows extraction curves for the multicomponent system (empty symbols). The extraction curve of the monocomponent system (filled symbols) has also been included for the sake of comparison. In the same direction that for the monocomponent system, the extraction of Na⁺ and K⁺, Mg²⁺, Ca²⁺ and Sr²⁺ was completely zero at any equilibrium pH value. Li⁺ remained the only cation extracted from an equilibrium pH higher than 9.0 with a 10 % extraction, reaching the maximum extraction value, 95.4 %, at a pH of 12.2, with or without the presence of Na⁺ and K⁺. These results provide shreds of evidence facing selective lithium extraction can be achieved by DBM•TOPO system in the presence of alkaline cations. Mention, that, the initial and equilibrium pH follow the same trend as in the case of monocomponent systems, as expected.

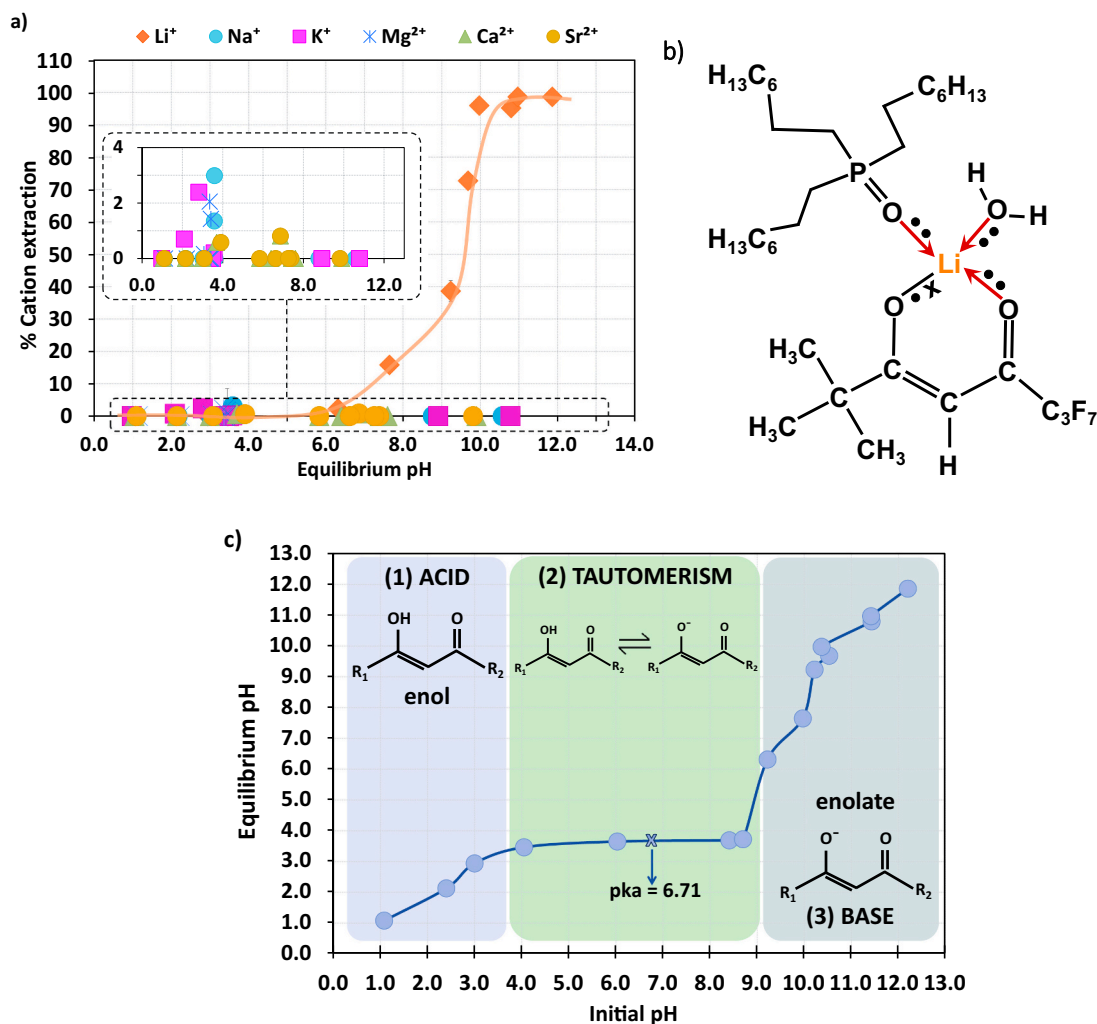


Fig. 8. a) Extraction percentage of the cations from monocomponent systems versus equilibrium pH, b) possible bonding mechanism of Li⁺•FDOD•TOPO, c) variation of the equilibrium pH versus the initial pH of the aqueous phase. [FDOD] = 0.03 mol L⁻¹; [TOPO] = 0.03 mol L⁻¹; O/A = 1; time of extraction = 10 min.

3.3.3. Cation extraction curves for FDOD•TOPO system

As in the previous section, with the best Li^+ extraction conditions obtained in Section 3.3.1, the individual extraction curves of Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} and Sr^{2+} , with the concentrations corresponding to the model brines of this work (indicated in Table 1), were performed with the extractants combination FDOD•TOPO for $[\text{FDOD}\bullet\text{TOPO}]/[\text{Li}^+] = 50$, represented in Fig. 8a, while Fig. 8b shows possible bonding mechanism of $\text{Li}^+\bullet\text{FDOD}\bullet\text{TOPO}$, and Fig. 8c shows the equilibrium and initial pH of the aqueous phase.

For FDOD•TOPO system alkaline cations Na^+ and K^+ and alkaline earth, Mg^{2+} , Ca^{2+} and Sr^{2+} were not extracted at any pH evaluated. Mg^{2+} , Ca^{2+} and Sr^{2+} were not assessed at an initial $\text{pH} > 9.8$. Li^+ shows the same trend, but in other ranges of pH and extraction percentage (Fig. 8a). At equilibrium pH 8.5 and 10.97, extracted Li^+ is around 25 % and 98.7 %, respectively, for FDOD•TOPO system, versus a 4 % and 80 %, respectively for DBM•TOPO system, namely, the extraction curve using FDOD•TOPO system is displaced towards the acid zone. Given both extractant, DBM and FDOD are β -diketones, their performance towards extraction of Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} and Sr^{2+} is based on the same phenomena, the tautomeric effect and charge density of each cation, as described in Section 3.3.2. Finally, the FDOD•TOPO system follows the same trend that DBM•TOPO system regarding the initial and equilibrium pH. Nevertheless, pH which extraction process starts is lower for FDOD•TOPO system ($\text{pH} = 7.0$) (Fig. 8a). As has been mentioned for DBM, β -diketones have an enol- and keto-forms (tautomerism mechanism). For FDOD, this behaviour was to be expected as each addition of fluorine atoms to β -diketone increases the acidic properties of the compound and thus improves its chelating characteristics over this pH range, thus facilitating proton exchange with Li^+ [44].

Along the same line that for DBM•TOPO system, the monocomponent and the multicomponent curves for FDOD•TOPO system and cations Li^+ , Na^+ , K^+ were jointly plotted (Fig. 9).

It can be observed as the cations have the same behaviour in both mediums; the negligible extraction of Na^+ and K^+ in the whole pH range studied, the increase of the Li^+ extraction with the equilibrium pH, reaching 98.7 % at a pH value of 11.0 (Fig. 9) and the same trend for equilibrium pH.

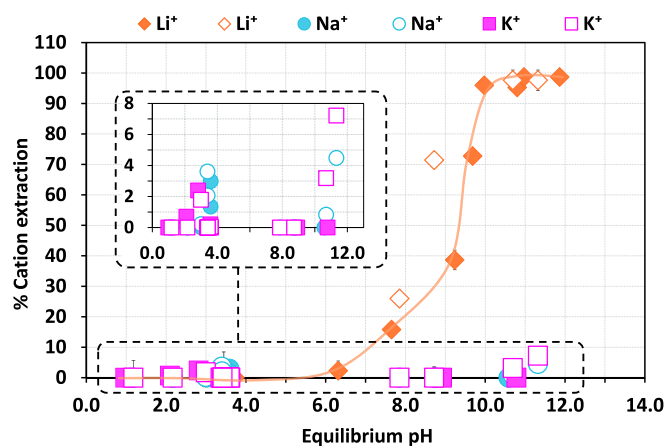


Fig. 9. Extraction percentage of the cations from monocomponent systems (filled) and multicomponent systems (empty). FDOD•TOPO. $[\text{FDOD}] = 0.03 \text{ mol L}^{-1}$; $[\text{TOPO}] = 0.03 \text{ mol L}^{-1}$; O/A = 1; time of extraction = 10 min.

4. Conclusions

In this work, the Li^+ selective separation from simulated seawater desalination concentrates, containing Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} and Sr^{2+} has been reached. β -Diketones and organophosphates have been validated as extractants, according to the results obtained in previous works via molecular simulation using ab initio Density Functional Theory.

At basic $\text{pH}_{\text{aq},i} = 12.0$, the DBM•TOPO and FDOD•TOPO systems were able to extract about 85 % and 93 % of Li^+ , respectively. Moreover, the selective separation is close to 100 % due to the negligible extraction of the Na^+ , K^+ , Mg^{2+} , Ca^{2+} and Sr^{2+} at any pH. The favorable extraction of Li^+ was explained by FT-IR analysis of the sample before and after the Li^+ extraction. At basic pH, a new band appeared in the spectrum of extraction, 1738 cm^{-1} , characteristic of an enol group confirmed the β -diketones tautomeric effect.

The DBM•TOPO system with the multicomponent mixture of the cations was able to extract a maximum of 95.4 % Li^+ at equilibrium $\text{pH} = 12.0$, whereas FDOD•TOPO reached 98.7 % at the equilibrium $\text{pH} = 10.97$. On the other hand, the rest of the cations were not extracted at the evaluated pH, which according to the literature, is due to the higher value of charge density (z/r) for lithium, compared to the rest of the cations. Besides, the best behaviour of FDOD•TOPO system versus DBM•TOPO was to be expected. The presence of electronegative fluorine atoms in the extractant enhances the acidic character of the molecule, facilitating proton exchange with Li^+ .

Finally, this study highlights the advantages of an extraction strategy that can recover selectively Li^+ from complex mixtures with competitive cations at higher concentrations like SWRO concentrates, and brings a promising method for lithium separation in such not conventional sources.

CRedit authorship contribution statement

E. Fernández-Escalante: Investigation, Conceptualization, Methodology, Writing – review & editing. **R. Ibañez:** Investigation, Conceptualization, Methodology, Writing – review & editing, Funding acquisition. **Ma.-F. San-Román:** Investigation, Conceptualization, Methodology, Formal analysis, Writing – review & editing, Supervision, Funding acquisition.

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.

Data availability

The data that has been used is confidential.

Acknowledgments

This research was developed in the framework of the projects PID2020-115409RB-I00, PDC2021-120786-I00 and TED2021-129874B-I00 financed by the Ministry of Science and Innovation (Spain). Elena Fernández-Escalante is grateful for the predoctoral contract PRE2021-100160.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.desal.2023.116525>.

References

- [1] M.O. Mavukkandy, C.M. Chabib, I. Mustafa, A. al Ghaferi, F. AlMarzooqi, Brine management in desalination industry from waste to resources generation, *Desalination* 472 (2019), <https://doi.org/10.1016/j.desal.2019.114187>.
- [2] International Desalination Association (IDA), *Desalination & Reuse Handbook 2021-2022*, 2022. <https://idadesal.org/>. (Accessed 8 November 2022).
- [3] U. Caldera, C. Breyer, Strengthening the global water supply through a decarbonised global desalination sector and improved irrigation systems, *Energy* 200 (2020), <https://doi.org/10.1016/j.energy.2020.117507>.
- [4] E. Jones, M. Qadir, M.T.H. van Vliet, V. Smakhtin, S. mu Kang, The state of desalination and brine production: a global outlook, *Sci. Total Environ.* 657 (2019) 1343–1356, <https://doi.org/10.1016/j.scitotenv.2018.12.076>.
- [5] A. Khalil, S. Mohammed, R. Hashaikheh, N. Hilal, Lithium recovery from brine: recent developments and challenges, *Desalination* 528 (2022), <https://doi.org/10.1016/j.desal.2022.115611>.
- [6] I. Ihsanullah, J. Mustafa, A.M. Zafar, M. Obaid, M.A. Atieh, N. Ghaffour, Waste to wealth: a critical analysis of resource recovery from desalination brine, *Desalination* 543 (2022), <https://doi.org/10.1016/j.desal.2022.116093>.
- [7] U. Geological Survey, MINERAL COMMODITY SUMMARIES 2019, 2019, <https://doi.org/10.3133/mcs2019>.
- [8] U. Geological Survey, MINERAL COMMODITY SUMMARIES 2022, 2022, <https://doi.org/10.3133/mcs2022>.
- [9] European Commission, COM 474. <https://op.europa.eu/s/nBRd>, 2020.
- [10] A. Kumar, G. Naidu, H. Fukuda, F. Du, S. Vigneswaran, E. Trioli, J.H. Lienhard, Metals recovery from seawater desalination brines: technologies, opportunities, and challenges, *ACS Sustain. Chem. Eng.* 9 (2021) 7704–7712, <https://doi.org/10.1021/acssuschemeng.1c00785>.
- [11] A. Yadav, P.K. Labhasetwar, V.K. Shahi, Membrane distillation crystallization technology for zero liquid discharge and resource recovery: opportunities, challenges and futuristic perspectives, *Sci. Total Environ.* 806 (2022), <https://doi.org/10.1016/j.scitotenv.2021.150692>.
- [12] U. Bardi, Extracting minerals from seawater: an energy analysis, *Sustainability* 2 (2010) 980–992, <https://doi.org/10.3390/su2040980>.
- [13] L. Zhang, L. Li, D. Shi, X. Peng, F. Song, F. Nie, Kinetics and mechanism study of lithium extraction from alkaline solution by HFTA and TOPO and stripping process using Lewis cell technique, *Sep. Purif. Technol.* 211 (2019) 917–924, <https://doi.org/10.1016/j.seppur.2018.10.043>.
- [14] G. Zante, M. Boltoeva, A. Masmoudi, R. Barillon, D. Trébouet, Highly selective transport of lithium across a supported liquid membrane, *J. Fluor. Chem.* 236 (2020), <https://doi.org/10.1016/j.jfluchem.2020.109593>.
- [15] G.R. Harvianto, S.H. Kim, C.S. Ju, Solvent extraction and stripping of lithium ion from aqueous solution and its application to seawater, *Rare Metals* 35 (2016) 948–953, <https://doi.org/10.1007/s12598-015-0453-1>.
- [16] P. Ortiz-Albo, S. Torres-Ortega, M. González Prieto, A. Urriaga, R. Ibañez, Techno-economic feasibility analysis for minor elements valorization from desalination concentrates, *Sep. Purif. Rev.* 48 (2019) 220–241, <https://doi.org/10.1080/15422119.2018.1470537>.
- [17] D. Shi, B. Cui, L. Li, M. Xu, Y. Zhang, X. Peng, L. Zhang, F. Song, L. Ji, Removal of calcium and magnesium from lithium concentrated solution by solvent extraction method using D2EHPA, *Desalination* 479 (2020), 114306, <https://doi.org/10.1016/j.desal.2019.114306>.
- [18] Z. Ren, X. Wei, R. Li, W. Wang, Y. Wang, Z. Zhou, Highly selective extraction of lithium ions from salt lake brines with sodium tetraphenylborate as co-extractant, *Sep. Purif. Technol.* 269 (2021), 118756, <https://doi.org/10.1016/j.seppur.2021.118756>.
- [19] J. Rydberg, M. Cox, C. Musikas, G.R. Choppin, *Solvent Extraction Principles and Practice*, 2nd edition, CRC Press, Florida, 2004.
- [20] Z. Li, K. Binnemans, Selective removal of magnesium from lithium-rich brine for lithium purification by synergetic solvent extraction using β -diketones and Cyanex 923, *AIChE J.* 66 (2020), e16246, <https://doi.org/10.1002/aic.16246>.
- [21] R. Coterillo, L.E. Gallart, E. Fernández-Escalante, J. Junquera, P. García-Fernández, I. Ortiz, R. Ibañez, M.F. San-Román, Selective extraction of lithium from seawater desalination concentrates: study of thermodynamic and equilibrium properties using density functional theory (DFT), *Desalination* 532 (2022), <https://doi.org/10.1016/j.desal.2022.115704>.
- [22] T. Kinugasa, H. Nishibara, Y. Murao, Y. Kawamura, K. Watanabe, Equilibrium and kinetics of lithium extraction by a mixture of LIX54 ad TOPO, *J. Chem. Eng. Jpn* 27 (1994) 815–818, <https://doi.org/10.1252/jcej.27.815>.
- [23] Y. Pranolo, Z. Zhu, C. Yong Cheng, Separation of lithium from sodium in chloride solutions using SSX systems with LIX 54 and Cyanex 923, *Hydrometallurgy* 154 (2015) 33–39, <https://doi.org/10.1016/j.hydromet.2015.01.009>.
- [24] L. Zhang, L. Li, H. Rui, D. Shi, X. Peng, L. Ji, X. Song, Lithium recovery from effluent of spent lithium battery recycling process using solvent extraction, *J. Hazard. Mater.* 398 (2020), 122840, <https://doi.org/10.1016/j.jhazmat.2020.122840>.
- [25] B. Swain, Separation and purification of lithium by solvent extraction and supported liquid membrane, analysis of their mechanism: a review, *J. Chem. Technol. Biotechnol.* 91 (2016) 2549–2562, <https://doi.org/10.1002/jctb.4976>.
- [26] P. Xu, J. Hong, X. Qian, Z. Xu, H. Xia, X. Tao, Z. Xu, Q.Q. Ni, Materials for lithium recovery from salt lake brine, *J. Mater. Sci.* 56 (2021) 16–63, <https://doi.org/10.1007/s10853-020-05019-1>.
- [27] T. Hanada, M. Goto, Synergistic deep eutectic solvents for lithium extraction, *ACS Sustain. Chem. Eng.* 9 (2021) 2152–2160, <https://doi.org/10.1021/acssuschemeng.0c07606>.
- [28] M. Ahmad, B. Garudachari, Y. Al-Wazzan, R. Kumar, J.P. Thomas, Mineral extraction from seawater reverse osmosis brine of gulf seawater, *Desalin. Water Treat.* 144 (2019) 45–56, <https://doi.org/10.5004/dwt.2019.23679>.
- [29] H. Valdés, A. Saavedra, M. Flores, I. Vera-Puerto, H. Aviña, M. Belmonte, Reverse osmosis concentrate: physicochemical characteristics, environmental impact, and technologies, *Membranes (Basel)* 11 (2021), <https://doi.org/10.3390/membranes11100753>.
- [30] M. Omerspahic, H. Al-Jabri, S.A. Siddiqui, I. Saadaoui, Characteristics of desalination brine and its impacts on marine chemistry and health, with emphasis on the Persian/Arabian gulf: a review, *Front. Mar. Sci.* 9 (2022), <https://doi.org/10.3389/fmars.2022.845113>.
- [31] Chemical Book, Chemical Book, 2022 (accessed October 20, 2022), https://www.chemicalbook.com/ProductIndex_EN.aspx.
- [32] L. Zhang, L. Li, D. Shi, X. Peng, F. Song, F. Nie, W. Han, Recovery of lithium from alkaline brine by solvent extraction with β -diketone, *Hydrometallurgy* 175 (2018) 35–42, <https://doi.org/10.1016/j.hydromet.2017.10.029>.
- [33] X.J. Pan, Z.H. Dou, T.A. Zhang, D.L. Meng, Y.Y. Fan, Separation of metal ions and resource utilization of magnesium from saline lake brine by membrane electrolysis, *Sep. Purif. Technol.* 251 (2020), 117316, <https://doi.org/10.1016/j.seppur.2020.117316>.
- [34] G.R. Harvianto, S.G. Jeong, C.S. Ju, The effect of dominant ions on solvent extraction of lithium ion from aqueous solution, *Korean J. Chem. Eng.* 31 (2014) 828–833, <https://doi.org/10.1007/s11814-014-0005-7>.
- [35] L. Zhang, D. Shi, L. Li, X. Peng, F. Song, H. Rui, Solvent extraction of lithium from ammoniacal solution using thenoyltrifluoroacetone and neutral ligands, *J. Mol. Liq.* 274 (2019) 746–751, <https://doi.org/10.1016/j.molliq.2018.11.041>.
- [36] X. Guo, S. Hu, C. Wang, H. Duan, X. Xiang, Highly efficient separation of magnesium and lithium and high-valued utilization of magnesium from salt lake brine by a reaction-coupled separation technology, *Ind. Eng. Chem. Res.* 57 (2018) 6618–6626, <https://doi.org/10.1021/acs.iecr.8b01147>.
- [37] V. Flexer, C.F. Baspineiro, C.I. Galli, Lithium recovery from brines: a vital raw material for green energies with a potential environmental impact in its mining and processing, *Sci. Total Environ.* 639 (2018) 1188–1204, <https://doi.org/10.1016/j.scitotenv.2018.05.223>.
- [38] R.M. Silverstein, F.X. Webster, *Spectrometric Identification of Organic Compounds*, Sixth Edition, 2005.
- [39] G. Zante, M. Boltoeva, A. Masmoudi, R. Barillon, D. Trébouet, Highly selective transport of lithium across a supported liquid membrane, *J. Fluor. Chem.* 236 (2020), 109593, <https://doi.org/10.1016/j.jfluchem.2020.109593>.
- [40] F. Vassallo, D. La Corte, N. Cancilla, A. Tamburini, M. Bevacqua, A. Cipollina, G. Micale, A pilot-plant for the selective recovery of magnesium and calcium from waste brines, *Desalination* 517 (2021), 115231, <https://doi.org/10.1016/j.desal.2021.115231>.
- [41] Y.-S. Kim, G. In, J.-M. Choi, Chemical equilibrium and synergism for solvent extraction of trace lithium with thenoyltrifluoroacetone in the presence of triethylphosphine oxide, *Bull. Kor. Chem. Soc.* 24 (2003) 1495–1500, <https://doi.org/10.5012/bkcs.2003.24.10.1495>.
- [42] T.v. Healy, Synergism in the solvent extraction of alkali metal ions by thenoyltrifluoroacetone, *J. Inorg. Nucl. Chem.* 30 (1968) 1025–1036, [https://doi.org/10.1016/0022-1902\(68\)80322-7](https://doi.org/10.1016/0022-1902(68)80322-7).
- [43] I. Itoh, M. Billah, T. Honjo, K. Terada, Separation and determination of a trace amount of lithium as its complex with 12-crown-4 by means of synergic extraction and flame thenoyltrifluoroacetone photometry, *Anal. Sci.* 7 (1991) 47–50, <https://doi.org/10.2116/analsci.7.Supple.47>.
- [44] F.G. Seeley, W.H. Baldwin, Extraction of lithium from neutral salt solutions with fluorinated/ β -diketones, *J. Inorg. Nucl. Chem.* 38 (1976) 1049–1052, [https://doi.org/10.1016/0022-1902\(76\)80027-9](https://doi.org/10.1016/0022-1902(76)80027-9).