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Liquid–liquid extraction of boron from continental brines by 2-butyl-1-octanol diluted in kerosene†

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Lithium production from brines generates significant quantities of salts, including boron, that are not effectively utilized and end up being stored in landfills. This study delves into a novel approach for directly extracting boron from native brines without performing solar evaporation as an alternative to traditional methods based on boron extraction from ores, offering a sustainable route to producing boric acid or borax. By exploring factors such as 2-butyl-1-octanol concentration, phase volume ratio, temperature, and pH, the research scrutinizes boron extraction efficiency from two native brines sourced from the salar de Hombre Muerto in Argentina, alongside a synthetic brine simulating these native compositions. Notably, the extractant demonstrates exceptional promise due to its limited solubility in the brine, measuring at just 18 mg L^{-1}. Optimal conditions—2 mol L^{-1} 2-butyl-1-octanol, O/A ratio of 4, 25 °C temperature, and pH of 5.5—resulted in a remarkable 98.2% and 94.2% recovery of boron from synthetic and native brines, respectively. Importantly, this extraction process showcased minimal co-extraction of lithium, calcium, magnesium, potassium, and sodium. Leveraging these findings, a proposed flowsheet outlines a highly selective method for extracting boron from brines, presenting an alternative avenue to conventional borax production from boron ores.

1. Introduction

Agriculture, glass, ceramic and detergent industries use 86% of the worldwide production of boron as boric acid (H_3BO_3) or borax ($Na_2B_4O_7 \cdot 10H_2O$).[1] Boron is also used in nuclear,[2] steel,[3] pharmaceutical,[4] catalysis,[5] hydrogen storage,[6] concrete,[7] textile[8] and military sectors.[9] Therefore, boron is classified as a strategic commodity in many countries, including the U.S. and the EU. Boron is mainly extracted from ores containing various minerals such as colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$), tincal ($Na_2B_4O_7 \cdot 10H_2O$), kernite ($Na_2B_4O_7 \cdot 4H_2O$) and ulexite ($NaCaB_5O_9 \cdot 8H_2O$) in which boron concentration can reach up to 15 wt%.[10] However, brines could be an alternative to minerals for boron production as they usually contain large amounts of boron. For instance, it is estimated that the salar de Uyuni (Bolivia) contains 3.2 million tons of boron.[11] Thus, boron extraction from brine could be a good alternative to ores as the exploitation of boron ores implies high energy consumption for crushing and grinding steps and the use of huge amounts of chemicals to leach ore concentrates.[12] Furthermore, the huge demand of lithium in the next decades due to the exponential increase of lithium-ion battery production for electric vehicles will be responsible for the co-extraction of a considerable amount of boron from brines, which should be valorised as co-product.

Many technologies were tested to extract boron from different types of aqueous solutions including precipitation,[13] (electro)-membrane operations,[14,15] solid–liquid extraction,[16] or liquid–liquid extraction.[17–20] Among them, liquid–liquid extraction is the most used technology in hydrometallurgy for the recovery of many metals including boron.[21,22] Alcohols[23–25] diluted in kerosene,[12] toluene,[26] chloroform,[19,25] benzene[27] or sulfonated kerosene[23,24,28,29] were extensively reported in the literature as extractants to recover boron from brines.

Brine evaporation in open air ponds is the most common technology in use today for lithium salts production from aqueous sources.[30] Boron needs to be removed from the concentrated brines in order to produce high purity lithium salts. Table 1 gathers the extraction and stripping conditions of boron processing from brines concentrated by solar evaporation for three companies. In 1998, the company Chemetall performed boron extraction from concentrated brine of the salar de Atacama (Chile) in lithium production plant.[31] Four mixers-settlers were implemented to extract boron at pH 2 by using 20% (vol.) isooctanol or 2-ethyl-1-hexanol diluted in kerosene. The pH of the brine was adjusted by adding hydrochloric acid and the phase volume ratio between the organic phase (O) and the aqueous phase (A) was O/A = 4. Boron

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Table 1 (a) Extraction and (b) stripping conditions of boron in the processes developed by (1) Chemetall company in 1998, (2) Minsal company in 2002, and (3) Anon *et al.* in 1996 (E_B: boron extraction efficiency in %, SE_B: boron stripping efficiency in %)

(a) Processes	Extractants	Diluents	T (°C)	O/A	E_B (%)	pH	Number of stages	Brines	Li loss (%)
(1) Chemetall	Isooctanol or 2-ethyl-1-hexanol, 20% (vol.)	Kerosene	—	4	99.0	2	4	Salar de Atacama concentrated	5–10
(2) Minsall	Isooctanol, 50% (vol.)	Kerosene	25	1	99.9	2	4	Salar de Atacama concentrated	10
(3) Anon *et al.*	2-Chloro-4(1,1,3,3)-tetramethylbutyl-6-methylol-phenol, 25% (vol.)	Kerosene	34	1.6	99.4	10	2	Searles lake	—

(b) Process	Stripping solution	T (°C)	O/A	SE_B (%)	Stage
(1) Chemetall	Water	—	—	100	4
(2) Minsall	0.02 mol L^{-1} NaOH or water	—	6	100	3
(3) Anon *et al.*	0.5 mol L^{-1} H$_2$SO$_4$	38	1	100	5

extraction efficiency reached 99% and the residual boron concentration was less than 2 mg L^{-1}, although 5–10% lithium was lost during boron extraction (see the brine composition before and after boron extraction in Table 2). Thereafter, boron was stripped from the loaded solvent with water or diluted sodium hydroxide by means of four mixers-settlers.

In 2002, boron was also extracted from concentrated brine containing 8 g L^{-1} boron from the salar de Atacama (Chile) by the Minsal company.[31] The extraction was performed with 50% (vol.) isooctanol in kerosene at O/A = 1 and 25 °C. The extraction efficiency of boron reached 99.9% by implementing four mixers-settlers but 10% lithium was lost.[31] The extraction solvent was regenerated in three stages with water or 0.02 mol L^{-1} sodium hydroxide (NaOH) at phase volume ratio O/A = 6.

The solubility of the extraction solvent in the brine and in the stripping solution were 200 mg L^{-1} and 2000 mg L^{-1}, respectively.

In the flowsheet reported in Fig. 1, boron was recovered and valorised as boric acid from the Searles lake brine (California, USA, composition reported in Table 3). The boron extraction plant was designed in 1996 to produce 150 tons per day of boric acid.[32] Boron processing started with boron extraction in two stages at 34 °C and O/A = 1.6. The extraction efficiency of boron reached 99.4% by contacting the extraction solvent containing 25% (vol.) 2-chloro-4-(1,1,3,3)tetramethylbutyl-6-methylol-phenol diluted in kerosene (flowrate of the extraction solvent = 12 100 L min^{-1}, flowrate of the native brine = 7380 L min^{-1}).

After extraction, the organic–aqueous phase mixture was sent to three lines of settlers where the two phases were separated. The solubility of the extraction solvent in the brine was 100 mg L^{-1} (pH = 8.9). The boron-depleted brine was sent to three parallel lines at 2460 L min^{-1} each, where the extraction solvent was removed as a froth or vapor in order to reduce the solvent solubility below 17 mg L^{-1} as recommended by the government,[32] before returning the boron-depleted brine to the lake. The extraction solvent recovered from the brine was collected and reused.

After extraction, 0.5 mol L^{-1} sulfuric acid was used to strip boron at O/A = 1 and 38 °C by using five mixer-settlers in counter-current. After stripping, the extraction solvent was washed with water so that it could be reused. The plant consumed about 75 700 L per day of concentrated sulfuric acid. Furthermore, 15 100 L of alcohol and 22 700 L of kerosene were needed each week to makeup the extraction solvent.

The boron-loaded stripping solution contained 6.1 wt% H$_3$BO$_3$, 2.8 wt% Na$_2$SO$_4$, 5.2 wt% K$_2$SO$_4$ as well as 10–15 mg L^{-1} extraction solvent due to solubility losses. The stripping solution was first sent through an adsorption column, filled with activated carbon, to remove the extraction solvent.

The activated carbon was regenerated in six-tray furnace at 650–760 °C. The boron-loaded stripping solution without extraction solvent was sent to two hemispherically-domed evaporator-crystallizers where it was joined by recycle sulfuric acid solution and circulated through titanium heat-exchanger tubes at 72 000 L min^{-1}. Water was evaporated at

Table 2 Composition of the concentrated brine from salar de Atacama (1) before boron extraction and (2) after boron extraction under the operating conditions reported in Table 1 for the Chemetall company

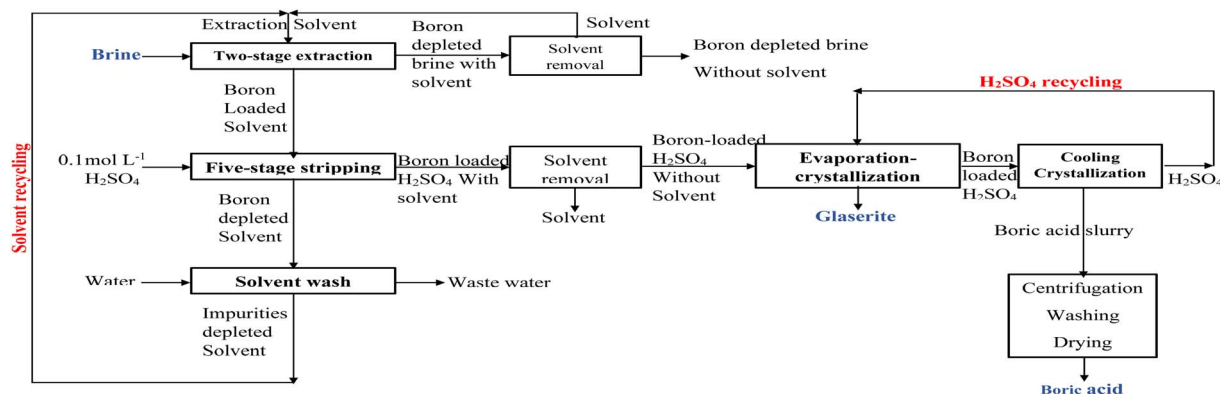|	Concentration (g L^{-1})							
	Li	Ca	Mg	B	Na	K	Cl$^-$	SO$_4^{2-}$
(1) Before boron extraction	63	0.53	12.9	7.3	0.8	0.19	358.6	0.16
(2) After boron extraction	60.3	0.51	12.9	0.001	0.73	0.18	344.6	0.19

Fig. 1 Flowsheet implemented to extract glaserite and boron from the Searles lake brine in U.S. (adapted from Garrett).[32]

Table 3 Composition of the Searles lake brine

Mineral	Content (wt%)
KCl	3.5
Na_2CO_3	6.5
$Na_2B_4O_7$	1.55
$Na_2B_2O_4$	0.75
Na_2SO_4	6
Na_2S	0.3
Na_3AsO_4	0.05
Na_3PO_4	0.1
NaCl	15.5
H_2O	65.72
WO_3	0.005
Br	0.071
Li_2O	0.009
I	0.002
F	0.001

65 °C, and salt cake and glaserite ($K_3Na(SO_4)_2$) were crystallized. They were removed, settled, and dewatered in solid bowl centrifuge. After the first stage of evaporation–crystallization, the overflow was then cooled at 35 °C in the second crystallization stage (flowrate = 83 300 L min^{-1}). Boric acid was crystallized, and the slurry withdrawn, settled, and dewatered in a four-stage pusher centrifuge. The solid was washed in two stages, and the overflow stripping solution depleted of boron was returned to the circuit. The boric acid cake was dried in a gas-fired rotary dryer and pneumatically transported to a storage silo. The purity of boric acid was 99.9% and contained only 0.05% SO_3 and 0.029% Na.

The nature of the extractant is particularly important in these processes as the extractant will control the efficiency of the process and the purity of the final product. In this work, preliminary experiments were performed to determine the solubility of extractants in the brine, the extraction efficiency of boron and the selectivity for boron towards sodium, lithium, magnesium, calcium and potassium for several extraction solvents composed of mono-hydroxy alcohols (1-octanol, 2-butyl-1-octanol and 2-ethyl-1-hexanol), or di-hydroxy alcohols (2-methyl-2,4-pentanediol, 2-ethyl-1,3-hexanediol and 2-butyl-2-ethyl-1,3-propanediol) diluted in kerosene or mixture of

kerosene and toluene. The highest extraction efficiencies of boron were obtained with di-hydroxy alcohols since 99% boron was extracted with 1 mol L^{-1} 2-ethyl-1,3-hexanediol diluted in 40 wt% kerosene + 60 wt% toluene at phase volume ratio O/A = 2 and pH = 5.5 while less than 55% boron was extracted with mono-alcohols. The best extraction efficiency with mono-alcohol was obtained by diluting 1 mol L^{-1} 2-butyl-1-octanol in kerosene and by performing the boron extraction at pH = 5.5 and O/A = 4.

Despite the high efficiency of diols for boron extraction, these alcohols cannot be used in industry for two main reasons. Firstly, their low solubility in kerosene requires the addition of highly toxic toluene to enhance their solubility. Secondly, they exhibit high solubility in water. For example, the solubility of 2-ethyl-1,3-hexanediol in brine is 70 times higher than that of 2-butyl-1-octanol. Furthermore, it has been observed that the selectivity of diols for boron over sodium, lithium, magnesium, calcium, and potassium significantly decreases under alkaline conditions. Therefore, it was decided to conduct a detailed investigation into the extraction properties of 2-butyl-1-octanol diluted in kerosene instead of diols diluted in toluene.

This work distinguishes itself within the field due to its focus on a novel approach to boron extraction from brines. Unlike conventional methods reliant on solar evaporation for brine concentration before extraction, the study targets direct boron extraction from native brines. Most future lithium production plants are anticipated to adopt technologies that bypass solar evaporation (direct lithium extraction), emphasizing the need to extract boron directly from these brines—a facet rarely explored in prior studies. The aim is to identify a highly efficient and selective extraction solvent capable of recovering and maximizing the value of boron as pure boric acid or borax, without relying on solar evaporation. This introduces a new pathway for obtaining top-quality boric acid or borax directly from brines, offering a supplementary approach to the prevalent method of boron extraction. Additionally, while solvent extraction for boron retrieval from brine has encountered challenges, notably concerning alcohol solubility within the brine leading to increased effluent treatment and extractant consumption, a crucial breakthrough has been uncovered. The selected alcohol demonstrates notably lower solubility in brine

Table 4 Composition, pH, ionic strength (I) and density at room temperature of native brine 1 (NB1), native brine 2 (NB2) and synthetic brine (SB). The ionic strength was determined by considering the speciation calculated with the Phreeplot software (databases: Pitzer and Minteq.V4)

Brine	pH	I (mol kg$_w^{-1}$)	Density (g cm^{-3})	Concentration (g L^{-1})									
				Li	Ca	Mg	B	Na	Sr	K	Fe	Cl$^-$	SO$_4^{2-}$
NB1	6.9	3.6	1.2	1.27	0.68	3.09	1.62	103.24	0.079	14.21	0.001	182.85	11.15
NB2	7.5	3.46	1.2	0.75	0.1	2.51	0.54	103.29	0	7.8	0	176.15	14.13
SB	5.5	3.6	1.2	1.27	0.68	3.09	1.62	103.24	0	14.21	0	182.25	8.78

compared to conventional boron extractants used in such processes, addressing a key limitation in this field. Moreover, the study breaks new ground by delving into the intricate physicochemistry of boron extraction by alcohols. Unlike previous research that often focused solely on the presence of boric acid in brines, the approach considers the complex boron speciation within the brine. This comprehensive analysis extends beyond boron to encompass the myriad of other elements present in the brine. The findings highlight the nuanced interplay between boron extraction, pH variations, and the co-extraction of elements like magnesium and calcium at different pH values. Consequently, our study contributes insights into the intricate physicochemical dynamics involved in boron extraction, elucidating its interactions with other impurities present in the brine.

In particular, this paper focuses on the use of 2-butyl-1-octanol diluted in kerosene to extract boron from a synthetic brine and two native brines from salar del Hombre Muerto, in northwest Argentina. It was shown that this extractant exhibits very low solubility in brine. The influence of 2-butyl-1-octanol concentration, phase volume ratio (O/A), pH and temperature on boron extraction and co-extraction of sodium, lithium, magnesium, calcium and potassium was systematically investigated. Boron stripping from the loaded organic phases was studied by considering three stripping solutions including hydrochloric acid, sodium hydroxide and deionized water. Finally, a simulation of continuous counter-current extraction of boron from these brines was performed and a flowsheet to extract selectively boron was proposed.

2. Experimental

2.1. Materials

Mono-hydroxy alcohols including 1-octanol (Oc, purity = 99%), 2-butyl-1-octanol (BOc, purity = 95%), 2-ethyl-1-hexanol (EH, purity = 99.6%), and di-hydroxy alcohols including 2-methyl-2,4-pentanediol (MPD, purity = 99%), 2-ethyl-1,3-hexanediol (EHD, purity = 97%) and 2-butyl-2-ethyl-1,3-propanediol (BEPD, purity = 99%), were purchased from Sigma-Aldrich (France). Kerosene (Low odour) was also provided by Sigma-Aldrich (France) while toluene (purity = 100%) was supplied by VWR (France).

Magnesium chloride (MgCl$_2$, purity = 98%, Sigma-Aldrich), calcium chloride (CaCl$_2$, purity = 90%, Sigma-Aldrich), boric acid (H$_3$BO$_3$, Sigma-Aldrich, purity = 99.5%), lithium sulfate (Li$_2$SO$_4$, Sigma-Aldrich, purity = 98.5%), sodium chloride (NaCl,

VWR, purity = 99.9%) and potassium chloride (KCl, VWR, purity = 99.5%) were dissolved in deionized water produced with the Puranity TU water system (VWR, resistivity = 18 MΩ cm) to prepare the synthetic brine mimicking the native brine which the composition is reported in Table 4.

The influence of the nature of the brine on the extraction properties of 2-butyl-1-octanol was investigated for two native brines from the Salar del Hombre Muerto (Argentina) referred to as native brine 1 (NB1) and native brine 2 (NB2) as well as a synthetic brine (SB) which the composition was the same as the composition of NB1 (Table 4). These brines were highly concentrated in monovalent elements (sodium, potassium and lithium) and divalent elements (calcium and magnesium). Iron and strontium were not accounted for preparing the synthetic brine as their concentrations were lower than 0.1 g L^{-1}. Hydrochloric acid (HCl, purity = 37%, Sigma-Aldrich) and sodium hydroxide (NaOH, purity = 99%, VWR) were used as received to adjust the pH of the synthetic brine.

2.2. Methods

2.2.1. Solvent extraction and stripping. A selection of mono and di-hydroxy alcohols were studied in preliminary experiments to determine their extraction efficiencies towards boron and their solubility in the brines. Results are shown in Table 5. 2-Butyl-1-octanol was selected for further investigations despite the low extraction efficiency (55%) because this extractant exhibits low solubility in the synthetic brine (SB) and it can be solubilized in kerosene without adding toluene. Batch solvent extraction experiments were carried out at 25 °C since no significant influence of the temperature on the extraction efficiency was observed at 25 °C, 35 °C, 40 °C and 50 °C in preliminary experiments. During the extraction tests, synthetic or native brines were mixed with the organic phase at different phase volume ratios (O/A) in centrifuge tubes (50 mL) or glass vessels (500 mL). The organic phases contained 2-butyl-1-octanol diluted in kerosene at different concentrations.

Organic and aqueous phases were contacted in centrifuge tubes during the extraction and the stripping experiments in a thermostated shaker (Gherardt Laboshake THL500/1) at 200 rpm for 4 hours and 2 hours, respectively. Preliminary experiments showed that the steady state was reached under these experimental conditions. It is expected that more intensive mixing/shaking will make the equilibrium to be reached faster. However, we chose to work under reproducible experimental conditions, and in this sense, a lab shaker did not provide intensive mixing, but it allowed for high

Table 5 Extraction efficiencies of boron (E_B) by alcohols in kerosene and kerosene + toluene, and solubilities (S_{alc}) of these alcohols in the synthetic brine (O/A = 2). Experimental conditions: pH = 5.5; temperature = 35 °C; alcohol concentration = 1 mol L^{-1}; extraction time = 4 hours. Oc: 1-octanol, BOc: 2-butyl-1-octanol, EH: 2-ethyl-1-hexanol, MPD: 2-methyl-2,4-pentanediol, EHD: 2-ethyl-1,3-hex-anediol, BEPD: 2-butyl-2-ethyl-1,3-propanediol

Kerosene			Kerosene + 60% (wt) toluene		
Alcohol	E_B (%)	S_{alc} (mg L^{-1})	Alcohol	E_B (%)	S_{alc} (mg L^{-1})
BOc	55	19	EHD	99	1368
EH	55	40	BEPD	97	259
Oc	32	43	MPD	96	12 603

reproducibility. Afterwards, the biphasic mixtures were centrifuged at 3000 rpm for 2 min by using a SIGMA 3–16 L centrifuge to separate the organic and the aqueous phases.

Finally, the aqueous droplets were removed from the organic phases by filtering with 0.20 μm minisart made of polypropylene (Sartorius, France) and the organic droplets were removed from the aqueous phases by filtering with 0.20 μm minisart made of regenerated cellulose (Sartorius, France).

The pH values of the aqueous phases were adjusted by adding 0.5 mol L^{-1} hydrochloric acid (HCl) or 2 mol L^{-1} sodium hydroxide (NaOH). After extraction, the boron-loaded organic phase was stripped with hydrochloric acid (HCl), sodium hydroxide (NaOH) or deionized water at O/A = 4 and 25 °C.

Extraction of boron from the synthetic brine (SB) and stripping tests of boron were performed in 500 mL glass vessels under stirring during 2 hours for the extraction tests and 1 hour for the stripping tests at 700 rpm by using a three-blade propeller (higher stirring was necessary to ensure good mixing in 500 mL-glass vessels). Then, the organic–aqueous phases mixtures were settled in 500 mL separating funnels for 30 min. For these tests, the extraction solvent was composed of 2 mol L^{-1} 2-butyl-1-octanol diluted in kerosene and 0.1 mol L^{-1} NaOH was used as stripping solution. All experiments were carried out at 25 °C and O/A = 4. The reproducibility of these experiments was checked by performing 10 times extraction and stripping tests in centrifuge tubes (see experimental conditions above) under the same experimental conditions. The same values for the extraction and the stripping efficiencies were obtained. The extraction and stripping equilibria were reached faster when the tests were performed in the glass vessels under stirring with a three-blade propeller at 700 rpm.

2.2.2. Analyses. Exactly 1 mL of aqueous phase was sampled and diluted in 2% (vol.) nitric acid prepared by dilution of 65% nitric acid (Sigma-Aldrich) in deionized water (resistivity = 18 MΩ cm). Elemental analyses of the samples were performed with a microwave plasma-atomic emission spectrometer (MP-AES model 4210, Agilent, France). The analyses were confirmed by inductively coupled plasma-optical emission spectroscopy (ICP-OES model 7400 Duo, Thermo Fisher Scientific, France). ICP standards containing 1000 mg L^{-1} of boron, potassium, magnesium, sodium, calcium and lithium were purchased from Sigma-Aldrich. The

samples were diluted 100 times and 1000 times in 2% (vol.) nitric acid for calcium analyses and for the other elements, respectively. It was inferred that chloride and sulfate ions were not significantly extracted during liquid–liquid extraction experiments, and therefore, their concentrations in the samples were the same as in brines. The matrix effect was avoided by adding appropriate concentrations of chloride, sulfate and sodium in the standards so that their concentrations matched with those found in the samples to analyze.[33–36] Chloride, sulfate and sodium concentrations in the matrixes were set by using hydrochloric acid (purity = 37%, Sigma-Aldrich), sulfuric acid (purity = 96%, Sigma-Aldrich) and 26 g L^{-1} sodium chloride, respectively. For MP-AES analyses, concentrations of lithium, boron, potassium, magnesium, calcium and sodium were determined at 670.784 nm, 249.677 nm, 766.491 nm, 518.360 nm, 393.366 nm and 568.820 nm, respectively. For ICP-OES analyses, the following wavelengths were used: 670.784 nm (lithium), 249.773 nm (boron), 769.896 nm (potassium), 279.553 nm (magnesium), 315.887 nm (calcium) and 589.592 nm (sodium).

Mass-balances were checked by performing quantitative elemental analyses in the stripping solution after full back-extraction from the organic phase.

Distribution ratio of the element e (D_e), extraction efficiency of the element e (E_e (%)), selectivity coefficient of the element e_1 towards the element e_2 (S_{e_1/e_2}) and stripping efficiency of boron (SE_B) were calculated as follows:

$$D_e = \frac{C_{e,org}}{C_{e,aq}} \quad (1)$$

$$E_e \ (\%) = \frac{C_{e,org} \times V_{org}}{C_{e,aq} \times V_{aq} + C_{e,org} \times V_{org}} \times 100 \quad (2)$$

where $C_{e,aq}$ and $C_{e,org}$ are the concentrations of the element e in the aqueous phase and in the organic phase at equilibrium, respectively. V_{org} and V_{aq} denote the volume of the organic and the aqueous phases, respectively.

By combining eqn (1) and (2), the extraction efficiency can be rewritten as follows:

$$E_e \ (\%) = \frac{D_e \times \nu}{1 + D_e \times \nu} \times 100 \quad (3)$$

where ν = O/A is the phase volume ratio between the organic and the aqueous phases (O and A stand for the organic phase volume and the aqueous phase volume, respectively).

The selectivity coefficient for e_1 towards e_2 was calculated as follows:

$$S_{e_1/e_2} = \frac{D_{e_1}}{D_{e_2}} \quad (4)$$

where D_{e_1} and D_{e_2} are the distribution ratios of element 1 and element 2, respectively.

The boron stripping efficiency (SE_B) was calculated as:

$$SE_B \ (\%) = \frac{C'_{B,aq} \times V'_{aq}}{C'_{B,org} \times V'_{org} + C'_{B,aq} \times V'_{aq}} \times 100 \quad (5)$$
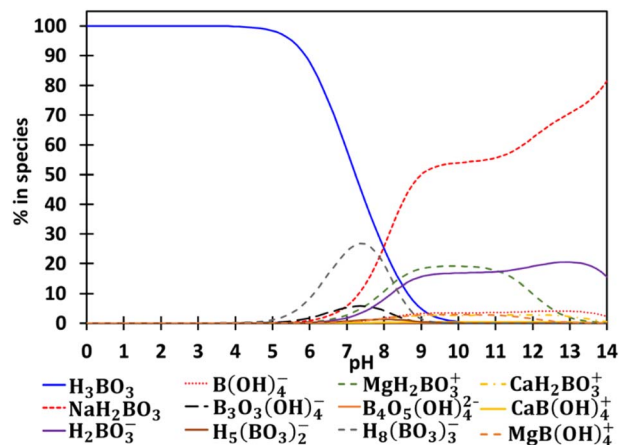
Fig. 2 Boron speciation *vs.* pH in the synthetic brine.

$C'_{B,aq}$ and $C'_{B,org}$ are the boron concentrations in the stripping solution and in the organic phase at equilibrium during the stripping step. V'_{org} and V'_{aq} represent the volume of the organic and the aqueous phases.

The error on the extraction and stripping efficiencies, and the error on the analytical method were estimated to be within 4% by repeating the experiments three times and by analysing the synthetic brine 10 times, respectively.

Dynamic viscosities of the organic phases before and after extraction were determined at 25 °C by using a Stabinger viscometer™ (Anton Paar SVM™ 2001). The viscometer was calibrated with the viscosity standards APN26, APS3, APN415 and APN7.5 provided by Anton Paar. Each sample was analysed twice. The viscometer cell was cleaned by rinsing with pure ethanol and dried with air after each viscosity measurement.

Water contents in organic phases after extraction were analysed by using a volumetric Karl Fisher Titrator (Mettler Toledo, France) after calibration with a standard containing 1% water (Sigma-Aldrich). These analyses were performed with HYDRA-NAL Composite 5 and Methanol Rapid (Sigma-Aldrich).

The solubilities of the alcohols (S_{alc}) in the aqueous phase after extraction were determined by Total Organic Carbon analyses (Shimadzu TOC-VCSH), as follows:

$$S_{alc} = \frac{(TOC_S - TOC_D)}{X} \tag{6}$$

where TOC_S is the total organic carbon of the solvent (alcohol + diluent), TOC_D is the total organic carbon of the diluent and X is the mass fraction of carbon in the alcohol.

2.3. Speciation calculations

Speciation diagrams were calculated with PhreePlot on a PC under Windows 11. PhreePlot is a charting and plotting extension of Phreeqc (version 3.7) for creating commonly needed types of diagrams.[37] The databases Pitzer and Minteq.V4 were used for speciation calculations. The relevant thermodynamic constants and the corresponding chemical reactions included in these databases are reported in Table S1 (ESI†).
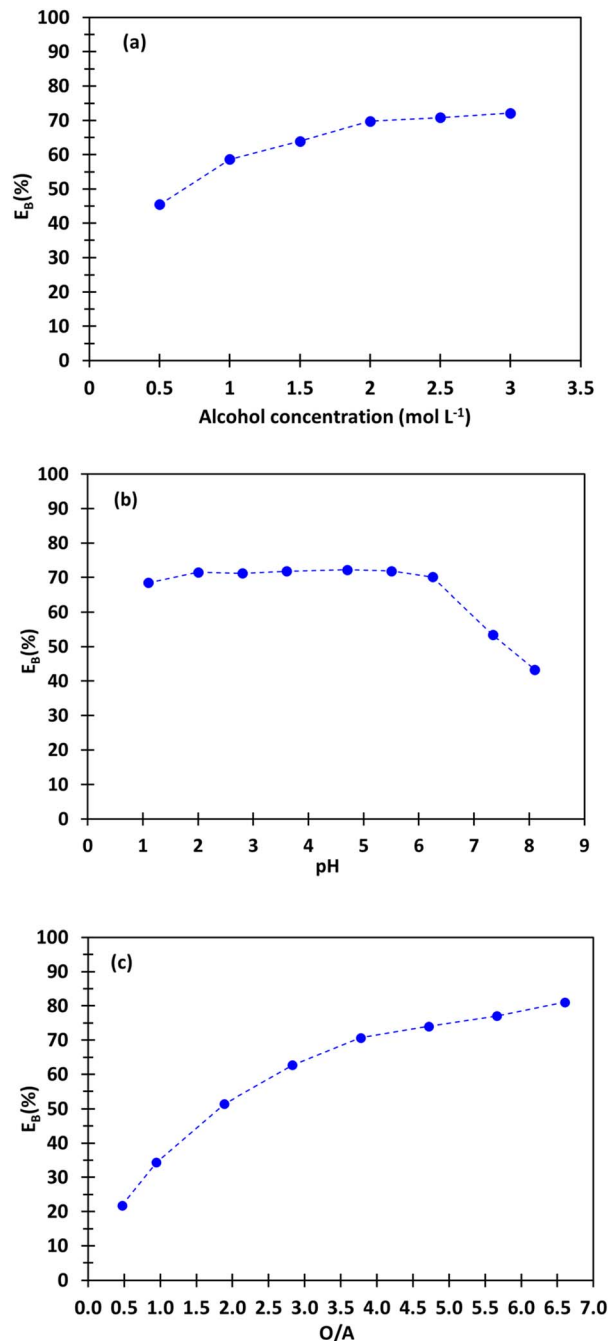

Fig. 3 Influence of (a) 2-butyl-1-octanol concentration in kerosene (O/A = 4, pH = 1, 25 °C), (b) pH (O/A = 4, extraction solvent: 2 mol L^{-1} 2-butyl-1-octanol, 25 °C) and (c) O/A (pH = 1, extraction solvent: 2 mol L^{-1} 2-butyl-1-octanol in kerosene, 25 °C) on boron extraction efficiency from the synthetic brine (SB).

3. Results and discussion

3.1. Speciation calculations

The speciation diagram of boron(III) in the synthetic brine is reported in Fig. 2 and the speciation diagrams of calcium(II), magnesium(II), potassium(I), sodium(I) and lithium(I) in the synthetic brine are gathered in Fig. S2–S6 (ESI†). These
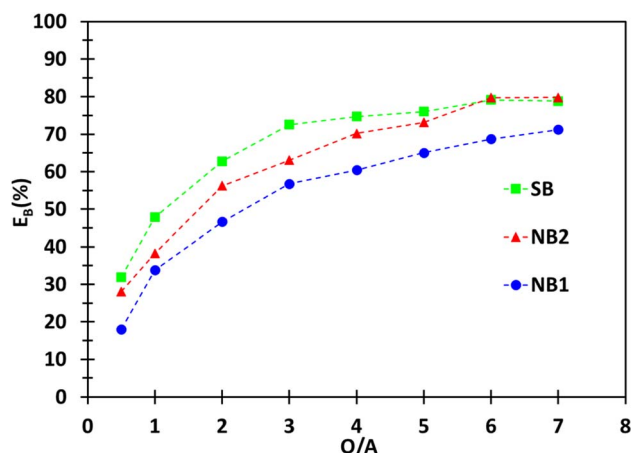
Fig. 4 Extraction of boron from the synthetic brine (SB) and the native brines (NB1 and NB2) at different phase volume ratios O/A (extraction solvent: 2 mol L^{-1} 2-butyl-1-octanol in kerosene, pH = 5.5 for SB, pH = 6.9 for NB1, pH = 7.5 for NB2, 25 °C).

calculations show that boron exists as boric acid until pH 9.5. At higher pH, borate and several polyborate species are formed in solution as well as calcium–boron and magnesium–boron species.

3.2. Boron extraction and impurities co-extraction

Fig. 3 shows the influence of the concentration of 2-butyl-1-octanol in kerosene, the phase volume ratio (O/A) and the pH at equilibrium on boron extraction efficiency from the synthetic brine at 25 °C. An increase of 2-butyl-1-octanol concentration is responsible for an increase of boron extraction efficiency. The curve in Fig. 3a shows that the extraction efficiency reaches a plateau (%E_B = 70) when 2-butyl-1-octanol concentration is greater than 2 mol L^{-1}.

No co-extraction of lithium, calcium magnesium, sodium and potassium was observed. Therefore, the other extraction tests were performed with 2 mol L^{-1} 2-butyl-1-octanol in kerosene.

Boron extraction efficiency does not depend on pH when pH values are lower than 5.5 (%E_B = 70, Fig. 3b). Above this value, an increase of pH is responsible for a sharp decrease of boron extraction efficiency. This significant decrease in the extraction efficiency of boron can be explained by the change in boron speciation as a function of pH (Fig. 2). At pH = 1–5.5, boron exists only as boric acid in solution, i.e. a non-charged species. Above pH 5.5, boric acid concentration in the brine decreases and is almost equal to zero at pH = 9.5. Indeed, boric acid is progressively converted into borate when pH increases. Borate anions react with magnesium, sodium and calcium to form magnesium borate, sodium borate and calcium borate (see Fig. 2), which are not extractable by 2-butyl-1-octanol as no co-extraction of magnesium, calcium and sodium is observed (2-butyl-1-octanol usually extracts neutral species including acids like boric acid).

Fig. 3c shows an increase of boron extraction efficiency when the phase volume ratio (O/A) increases as it is expected according to eqn (3). Around 22% of boron is extracted at O/A = 0.5, extraction reaches 70% at O/A = 4, and even 81% at O/A = 6.6 when the pH at equilibrium is the same and equal to 1. However, O/A = 4 seems to be a good compromise to achieve high extraction efficiency even at moderate flowrate of the extraction solvent.

Fig. 4 compares the influence of the phase volume ratio (O/A) on boron extraction efficiency for the synthetic brine (SB) and the native brines (NB1 and NB2) under the previous optimal experimental conditions (extraction solvent: 2 mol L^{-1} 2-butyl-1-octanol in kerosene, pH = 5.5 for SB, pH = 6.9 for NB1, pH = 7.5 for NB2, temperature = 25 °C).

Despite the difference in chemical composition of the brines, Fig. 4 shows that the extraction curves for the synthetic brine (SB) and the native brine 2 (NB2) are very similar. Surprisingly, the extraction curves obtained for SB and NB1 are different even though both brines have similar compositions. This difference may be due to the water activity of the brines that are not necessarilythe same, and/or the different values of pH between the two brines since pH influences the extraction efficiency at pH greater than 5.5 (Fig. 3b).

Under the optimal extraction conditions, i.e. 2 mol L^{-1} 2-butyl-1-octanol in kerosene, pH = 5.5, O/A = 4 and 25 °C, 10 extraction tests from SB were performed with glass vessels. The average values of boron extraction efficiency was 66 ± 3%.

This investigation shows a high selectivity of boron extraction from brine under the optimal conditions mentioned above which leads to provide high purity boron salt when boron is co-valorised in the plants.

3.3. Boron stripping

Around 20 mL of boron-loaded organic phase was prepared for stripping tests by contacting 5 mL of the synthetic brine SB with 20 mL of extraction solvent under the optimal extraction conditions, i.e. 2 mol L^{-1} 2-butyl-1-octanol diluted in kerosenes at O/A = 4, pH 5.5 and 25 °C. Boron extraction experiments from SB were repeated 6 times the average extraction efficiency was 72 ± 1%. Boron concentration and water content in the organic phase after extraction were 0.024 mol L^{-1} and 0.3 wt%, respectively.

Fig. 5 shows the effect of the nature of the stripping solution (0.2 mol L^{-1} sodium hydroxyde (NaOH), 0.2 mol L^{-1} hydrochloric acid (HCl) and deionized water) on the stripping efficiency at O/A = 4 and 25 °C. The stripping efficiency of boron follows this order: NaOH (100%) ≫ HCl (54%) ≳ H$_2$O (50%). The use of sodium hydroxide may destabilize the complex in the organic phase by favoring the formation of borate, which has no affinity towards 2-butyl-1-octanol (Fig. 2 and 3b). Low stripping efficiency with hydrochloric acid was expected as low pH favours the formation of boric acid, which is highly extractable by 2-butyl-1-octanol. However, the co-extraction of chloride as hydrochloric acid by 2-butyl-1-octanol via hydrogen bond formation could explain that the stripping efficiency is still significant since the competition between boric acid extraction and hydrochloric acid extraction favours boron stripping. The stripping efficiencies of boron with hydrochloric acid and water are similar. Such a result cannot be explained by water
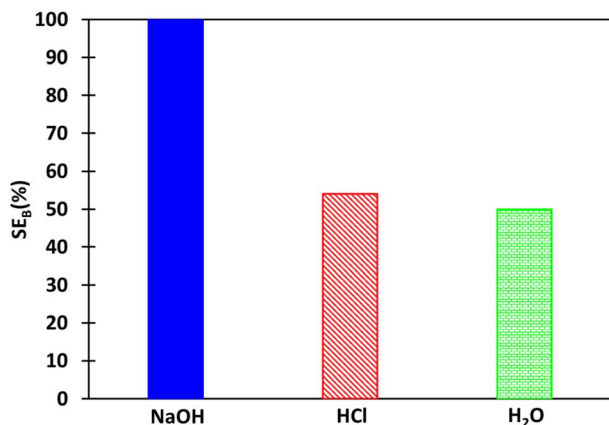
Fig. 5 Boron stripping efficiency when 0.2 mol L^{-1} sodium hydroxide (NaOH), 0.2 mol L^{-1} hydrochloric acid (HCl) and deionized water are used as stripping solutions (O/A = 4, 25 °C). The organic phase was previously loaded by contacting the extraction solvent (2 mol L^{-1} 2-butyl-1-octanol diluted in kerosene) with the synthetic brine (SB) at O/A = 4, pH = 5.5 and 25 °C.
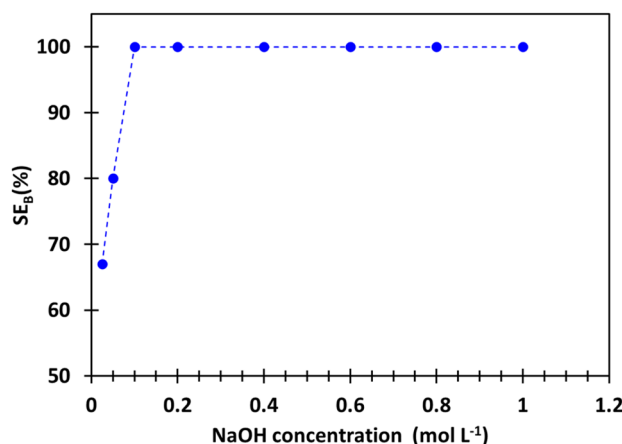

Fig. 6 Influence of sodium hydroxide concentration on boron stripping efficiency (O/A = 4, 25 °C). The organic phase was previously loaded by contacting the extraction solvent (2 mol L^{-1} 2-butyl-1-octanol diluted in kerosene) with the synthetic brine (SB) at O/A = 4, pH = 5.5 and 25 °C.
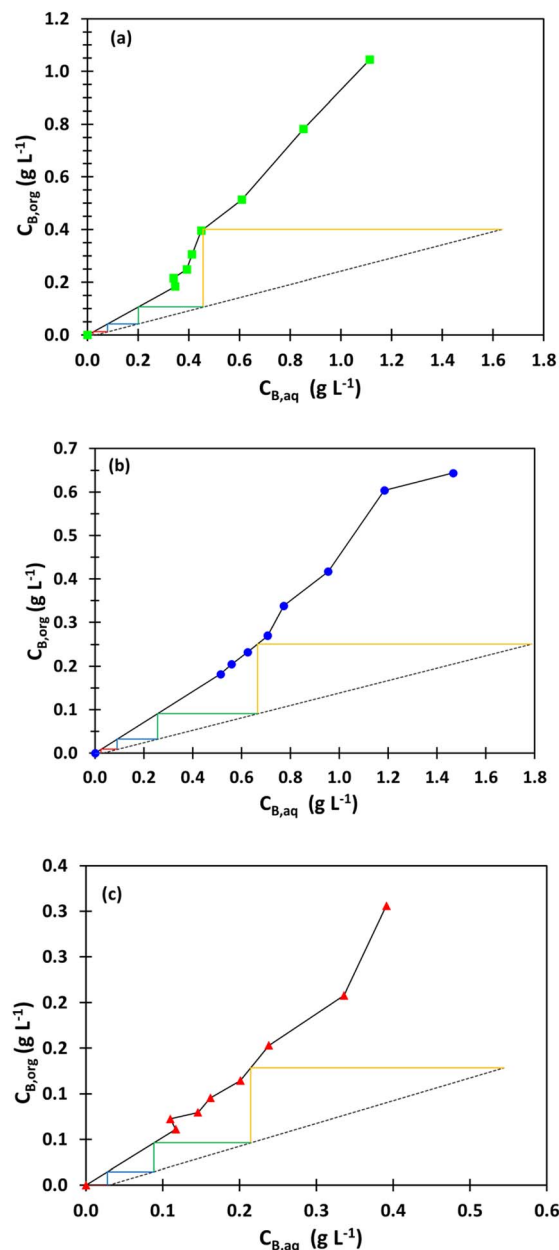

Fig. 7 McCabe–Thiele diagrams for boron extraction from (a) the synthetic brine (SB) with O/A = 4, (b) the native brine 1 (NB1) for O/A = 4 and (c) the native brine 2 (NB2) with O/A = 4.

extraction as only 0.3% (wt) of water is extracted by 2 mol L^{-1} 2-butyl-1-octanol diluted in kerosene. Indeed, 0.3% (wt) of water in the organic phase is not enough to destabilize the interactions between boron and 2-butyl-1-octanol in the organic phase.

Fig. 6 shows boron stripping efficiency increases when sodium hydroxide concentration increases. Full stripping is achieved with 0.1 mol L^{-1} sodium hydroxide and no increase of stripping efficiency is observed above this concentration. After stripping with 0.1 mol L^{-1} sodium hydroxide, the water content in the organic phase and the solubility of 2-butyl-1-octanol in the stripping solution were 0.4% (wt) and 181 mg L^{-1}, respectively. The solubility of 2-butyl-1-octanol in the stripping solution (181 mg L^{-1}) is much lower than that reported by Garrett *et al.*[31] (2000 mg L^{-1}). Such a low value of 2-butyl-1-octanol solubility in the stripping solution avoids the use of activated

carbon to reduce its concentration and avoid additional operating and capital costs for the effluent treatment.

In order to study the reproducibility of boron stripping from the loaded extraction solvent, 10 stripping tests were performed with 0.1 mol L^{-1} sodium hydroxide at O/A = 4 and 25 °C. The average value of boron stripping efficiency was 95 ± 5%.

Finally, it should be highlighted that boron is fully strip in one stage from the loaded organic phase by 0.1 mol L^{-1} NaOH at O/A = 4 and 25 °C. Furthermore, alcohol solubility is very low in the effluent, which avoid the implementation of expensive effluent treatment to remove organic matter from the stripping solution and allows the production of pure borax.
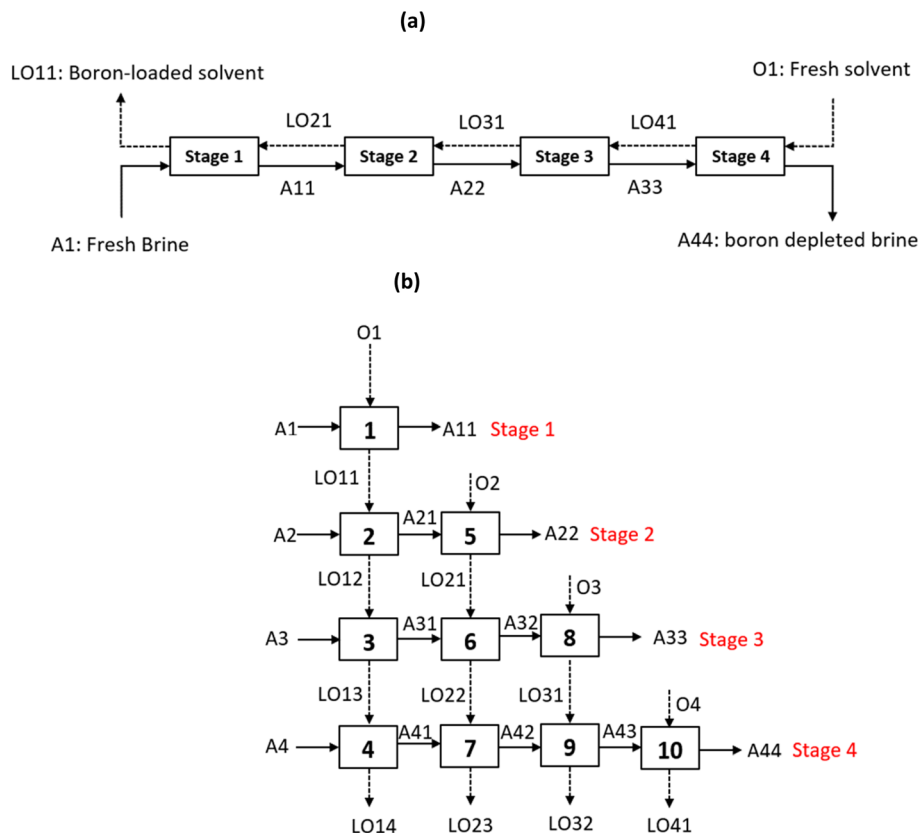
Fig. 8 Simulation model for counter-current extraction of boron from synthetic (SB) and native brine 2 (NB2) using 2 mol L^{-1} 2-butyl-1-octanol diluted in kerosene (O/A = 4; pH = 7.5). LO: loaded organic phase, A: aqueous phase.

Table 6 Boron extraction efficiency in each stage of four-stage continuous counter-current extraction for the synthetic brine (SB) and the native brine 2 (NB2) (extractant = 2 mol L^{-1} 2-butyl-1-octanol, diluent = kerosene, O/A = 4, 25 °C)

	E_B (%)	
Stage	Synthetic brine (SB)	Native brine 2 (NB2)
1	70	46.4
2	82.2	63.1
3	92.4	78.6
4	98.2	94.2

3.4. Flowsheet for boron extraction

The boron concentration in the boron-depleted brine was set at 25 mg L^{-1} for McCabe–Thiele simulation as Brown *et al.*[38] reported that boron concentration in brines should be less than 25 mg L^{-1} to guarantee the production of high-grade lithium carbonate for lithium-ion batteries. The McCabe–Thiele method was used to determine the number of mixers-settlers needed for boron extraction from the different brines (SB, NB1 and NB2) under optimal experimental conditions.

A phase volume ratio of O/A = 6 was required to remove boron from SB and NB2 whereas O/A = 9 should be necessary to remove boron from NB1 (see Fig. S7 in ESI†).

Fig. 7 shows that four mixers-settlers are needed at O/A = 4 to extract boron from SB and NB2 so that less than 25 mg L^{-1} of boron remain in the effluent.

The same number of mixers-settlers can be used to process the native brine 1 (NB1) provided that O/A = 7. It is indeed necessary to increase O/A to extract boron efficiently from NB1 because the boron extraction efficiency from this brine is lower since the natural pH of NB1 (pH = 6.9) is higher than the pH of SB (pH = 5.5). Under the same extraction conditions, no significant difference in the extraction efficiency of boron for both synthetic brine (SB) and native brine 1 (NB1) was observed. For instance, when boron is extracted from SB or NB1 with 2 mol L^{-1} 2-butyl-1-octanol diluted in kerosene at 25 °C, O/A = 4 and pH = 6.9, boron extraction efficiency reaches 60.5% (see extraction efficiency of boron under the extraction conditions mentioned above in Fig. 3b for SB and in Fig. 4 for NB1). Therefore, simulation of counter current extraction of boron from the brine following the model reported in Fig. 8 was performed to determine boron extraction efficiency in each stage when 2 mol L^{-1} 2-butyl-1-octanol diluted in kerosene was contacted with only the synthetic brine (SB) at pH 5.5 or the native brine 2 (NB2) at pH 7.5 and O/A = 4 (Table 6).

The simulation shows that the use of three stages leads to 92.4% and 78.6% of boron extraction efficiency and the addition of one more stage increases the extraction efficiency to 98.2% and 94.2% when the feed solution is the synthetic brine

Table 7 Composition, pH and density of the synthetic brine (SB) before extraction and after extraction (extractant = 2 mol L^{-1} 2-butyl-1-octanol, diluent = kerosene, O/A = 4, 25 °C)

Synthetic brine	pH	Density (g cm^{-3})	Concentration (g L^{-1})							
			Li	Ca	Mg	B	Na	K	Cl$^-$	SO$_4^{2-}$
Before extraction	5.5	1.2	1.27	0.68	3.09	1.62	103.24	14.21	182.25	8.78
After extraction	6.8	1.2	1.27	0.68	3.09	0.025	103.24	14.21	181.77	8.76
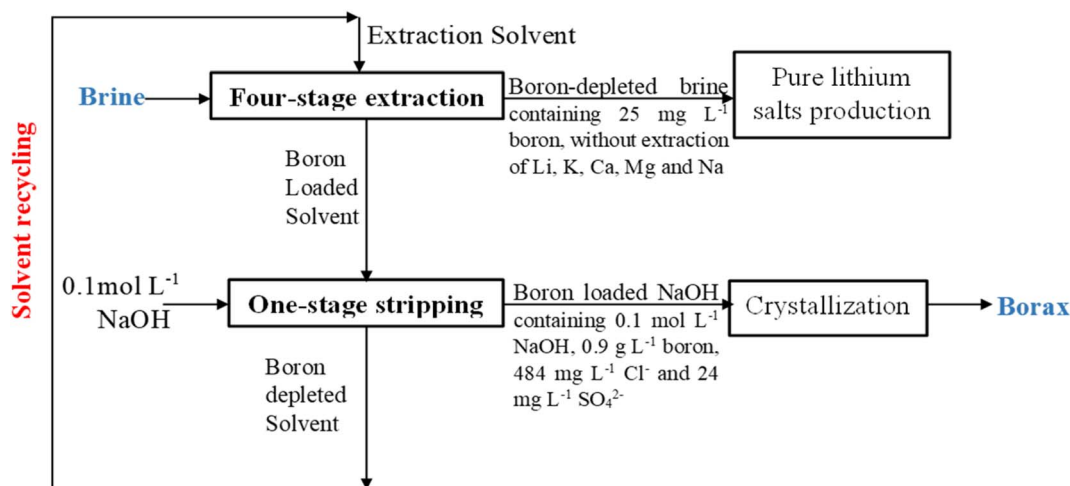
Fig. 9 Flowsheet for boron extraction from brine.

and the native brine 2, respectively. Therefore, the implementation of three mixers-settlers is enough to extract boron from the synthetic brine whereas 4 mixers-settlers are required to extract boron from the native brine 2.

Under these conditions (2 mol L^{-1} 2-butyl-1-octanol diluted in kerosene contacted with the synthetic brine (SB) at pH 5.5 or the native brine 2 (NB2) at pH 7.5 and O/A = 4), the solubility of 2-butyl-1-octanol in SB was 18 mg L^{-1} and the dynamic viscosity of the organic phase after extraction was very close to the viscosity before extraction, *i.e.* 4.4 mPa s. Furthermore, it is important to highlight that, under these experimental conditions, the solubility of 2-butyl-1-octanol in the brine (18 mg L^{-1}) is much lower than those reported in the literature[31,32] (solubility between 100 mg L^{-1} and 200 mg L^{-1}). Even if the initial concentration of boron was 1.60 g L^{-1} and 0.54 g L^{-1} in SB and NB2, respectively, it is interesting to point out that the residual concentration of boron in the brine was 25 mg L^{-1} in the last stage, as expected. Boron extraction was highly selective since no co-extraction of lithium, magnesium, calcium, sodium and potassium was observed. Long-chain mono-alcohols like heptanol, octanol, nonanol, and decanol have the capacity to extract hydrochloric acid or sulfuric acid by forming hydrogen bonds with the alcohol functional group. In this study, Table 7 does not demonstrate significant sulfate extraction, likely due to the brine's high pH value, as indicated by the negligible decrease in sulfate concentration after boron extraction. Conversely, Table 7 exhibits a slight extraction of chloride anions through the

formation of hydrogen bonds between HCl and the alcohol functional group. This is evident from the decrease in chloride concentration following boron extraction, accompanied by a pH increase from 5.5 to 6.8. It's worth noting that the chloride extraction observed here is less significant compared to the findings by Garrett *et al.*[31] (Table 2).

4. Conclusion

A potential method for extracting boron from brines involves using a 2 mol L^{-1} solution of 2-butyl-1-octanol in kerosene as the extraction solvent. Unlike previous industrial processes, this extractant has low solubility in brine (18 mg L^{-1}), allowing easy removal using activated carbon adsorption. It shows good boron extraction efficiency, especially in counter-current continuous mode, and demonstrates high selectivity for lithium, calcium, magnesium, potassium, and sodium.

Importantly, this method enables direct boron extraction from native brines without needing to concentrate the brine *via* evaporation. In one instance, using four stages, it removed 94.2% of boron from salar del Hombre Muerto (Argentina) brine without adjusting its pH, at an O/A ratio of 4. The boron is fully recovered from the loaded organic phase using a stripping solution containing 0.1 mol L^{-1} NaOH, allowing subsequent crystallization as borax.

This boron extraction process can precede direct lithium extraction (DLE) or the classic solar evaporation method, as

depicted in Fig. 9, allowing co-valorization of boron with lithium. This co-production of lithium salts alongside boron products like borax or boric acid reduces waste generation, offering environmental benefits.

Traditionally, boron was extracted from brines using commercial alcohols like isooctanol, 2-ethyl-1-hexanol, or 2-chloro-4 (1,1,3,3)-tetramethylbutyl-6-methylol-phenol. However, these alcohols had high solubility in both brine and stripping solutions. Therefore, finding efficient and appropriate molecules for boron recovery from native brines is crucial.

This study highlights that an extraction solvent comprising 2 mol L^{-1} 2-butyl-1-octanol diluted in kerosene exhibits efficient extraction, selectivity, and stripping properties for boron. Its low solubility in both brine and the stripping solution is a significant advantage. However, researchers have also suggested that using highly hydrophobic alcohols might further minimize solubility in these solutions. They showed that the length of aliphatic alcohols, the number of alcohol functional groups, and the branching of alkyl groups significantly impact solubility.[19,39]

Author contributions

Conceptualization: AC, AFK; formal analysis: AFK, AC, JM; funding acquisition: AC; investigation: AFK; software: AFK; project administration: AC; supervision: AC, VF; visualization: AFK, AC; writing-original draft: AFK, AC; writing-review and editing: AFK, AC, VF, JM.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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