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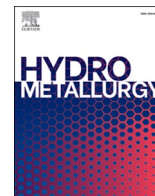
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Boron extraction by aliphatic mono- and di-hydroxy alcohols from a representative continental brine

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ABSTRACT

The extraction properties of mono-hydroxy alcohols (2-butyl-1-octanol, 2-ethyl-1-hexanol, 1-octanol) and di-hydroxy alcohols (2-ethyl-1,3-hexanediol, 2-butyl-2-ethyl-1,3-propanediol, 2-methyl-2,4-pentanediol) towards boron, potassium, lithium, sodium, calcium and magnesium ions were investigated as a function of pH and phase volume ratio (O/A) by considering an aqueous phase with a composition mimicking the brine from the Salar de Hombre Muerto in Argentina, in the Lithium Triangle. The mono-hydroxy alcohols are soluble in kerosene and sulfonated kerosene whereas the di-hydroxy alcohols are only soluble in mixtures of kerosene and toluene or *m*-xylene. No significant effect of the diluent on the extraction properties is observed. All alcohols exhibit high selectivity for boron over potassium, lithium, sodium, calcium and magnesium at acidic pH (pH = 1–5.5). A significant decrease of the extraction efficiency of boron by the mono-hydroxy alcohols is observed at pH >5.5 while no significant decrease of the extraction efficiency occurs with di-hydroxy alcohols. Finally, the best conditions to selectively extract boron from the synthetic brine with 1 mol L⁻¹ mono-hydroxy alcohols or di-hydroxy alcohols at 35 °C are pH = 5.5 and O/A = 4 when the diluent is kerosene and O/A = 2 when the diluent is a mixture of kerosene and toluene.

1. Introduction

Boron is used in agriculture, glass, ceramic, detergent and textile industries (Hilal et al., 2011; Turkbay et al., 2022; Zhang, 2021; Zhang et al., 2019). Nowadays, it is progressively used to produce materials for nuclear applications (Nasseri, 2018), military applications (Harussani et al., 2022), concrete (Kharita et al., 2011) and steel industries (Eichler and Lesniak, 2008), pharmaceutical industry (Ali et al., 2020), catalysis (*Borophene and Boron-Based Nanosheets: Recent Advances in Synthesis Strategies and Applications in the Field of Environment and Energy - Chand, 2021*) and for hydrogen storage (Chettri et al., 2021; Moussa et al., 2013; Panigrahi et al., 2020). Its demand is increasing with the development of industrial activities and new technologies. Around 12 million tons were produced from mining in 2016 (Turkbay et al., 2022) whereas a large amount of boron could be potentially extracted from brines as salar brines contain up to 4000 mg L⁻¹ (Garrett, 1998a). Continental brines are an alternative source since boron extraction from ores is expensive, energy and material intensive due to the beneficiation steps and the large amount of sulfuric acid used for leaching (Balinski et al., 2021). Presently, only two out of five facilities co-valorize boron and

lithium from brine by solar evaporation (Vera et al., 2023; Garrett, 1998b; Garrett, 1998c). When boron is not co-valorized, boron is stored in stockpiles with potential environmental impacts (Vera et al., 2023). From an economic and ecological viewpoint, it is therefore of great importance to include a boron recovery stage in the lithium production plants.

Many papers investigated solid/liquid extraction (adsorption, ion exchange resin (Guan et al., 2016; Gazi and Bicak, 2007)), (electro)-membrane operation (electrodialysis, reverse osmosis (Melnik et al., 1999; Farhat et al., 2013)), chemical precipitation (Shih et al., 2014) and liquid-liquid extraction (Bicak et al., 2005; Joshi et al., 2012; Karakaplan et al., 2004; Brooks et al., 2018) to recover boron from various aqueous solutions including wastewater and brines (Kim et al., 2023). Electrodialysis, ion exchange resins and chemical precipitation are not highly selective towards boron (Xu et al., 2021; Peng et al., 2021). Adsorption requires many stages and consumes an important amount of fresh water (Bonin et al., 2021). Reverse osmosis is an expensive technology that suffers from membrane ageing, especially when highly saline brines are processed. Conversely, solvent extraction is promising as it is a mature, efficient and relatively inexpensive technology, which has

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already demonstrated its applicability at industrial scale, including for boron extraction from brines (Chagnes, 2020; Garrett, 2004a). However, a significant lithium loss can occur during the solvent extraction of boron from brines. For instance, boron extraction from the Salar de Atacama (Chile) by 50% (vol.) isooctanol in kerosene at O/A = 1 and 25 °C can reach 99.9% by implementing 4 mixers-settlers but 10% of lithium is lost (Garrett, 2004a).

In order to reduce the capital expenditure and the operating costs, it is necessary to achieve high extraction efficiency and high selectivity at pH close to the natural pH of brines (pH ~ 7). Table 1 gathers the main solvent extraction systems reported in literature for boron extraction. Among the extractants listed in Table 1, alcohols appear as the most relevant for the recovery of boron from brines as high extraction efficiency is reached (99%). In most cases, boron is extracted from pure boric acid solution, low salinity synthetic brines or brines concentrated by evaporation, and a highly acidic pH is required to achieve high boron extraction efficiency from these brines. Aliphatic alcohols can be classified into two groups including mono-hydroxy alcohols and di-hydroxy alcohols. From brine concentrated by evaporation, Xu et al. (2021) (Xu et al., 2021) studied the extraction properties of boron by mono-hydroxy alcohols including *n*-decanol, *n*-octanol, isooctanol, 2-ethyl-1-hexanol, 2-octanol, 3,5,5-trimethyl-1-hexanol, isodecanol, 2-propyl-1-heptanol and isotridecanol diluted in sulfonated kerosene. The highest boron extraction efficiency (99%) was obtained with 3 stages at a phase volume ratio O/A = 1 by contacting the brine concentrated by evaporation from the East Taijinar Salt Lake (pH adjusted to 3.5) with an organic phase containing 2.5 mol L⁻¹ isodecanol diluted in sulfonated kerosene. However, the selectivity towards other brine constituents was not studied (calcium, magnesium, sodium, lithium and potassium). Balinski et al. (2021) (Balinski et al., 2021) also investigated the extraction properties of boron from a synthetic boric acid solution by mono-hydroxy alcohols (*n*-octanol, 2-ethyl-1-hexanol, 2-butyl-1-octanol, 2-octanol and 3,7-dimethyl-3-octanol). At pH = 2 and O/A = 2, the highest extraction efficiency for boron reached only 41% by using 6 mol L⁻¹ 2-ethyl-1-hexanol in kerosene. Peng et al., 2021 and Guo et al. (2020a) reported that >99% of boron was extracted from Xitajiner (Qaidam basin in China) salt lake brine with two mixers-settlers by using 2,2,4-trimethyl-1,3-pentanediol diluted in tetrachloromethane or sulfonated kerosene. However, the selectivity of these extraction solvents was not investigated.

Karakaplan et al. (2003) synthesized nine 1,3-di-hydroxy alcohols to investigate the influence of their chemical structure on boron extraction efficiency from an aqueous solution containing 0.01 mol L⁻¹ boric acid, 0.49 mol L⁻¹ sodium chloride and 0.01 mol L⁻¹ hydrochloric acid (ionic strength remained constant and equal to 0.5 mol L⁻¹). Among these alcohols, 0.5 mol L⁻¹ of 2-methyl-3-benzyl-1,3-butanediol diluted in

chloroform exhibited the greatest boron extraction efficiency (95%) at pH 2 (phase volume ratio O/A = 1). It was found that 1,3-di-hydroxy alcohols containing 6–12 carbon atoms and small alkyl groups (i.e. methyl, ethyl, benzyl) at the vicinity of the alcohol function exhibit the highest boron extraction efficiency.

In this paper, the extraction properties of the most relevant alcohols reported in Table 2 towards boron, potassium, lithium, sodium, calcium and magnesium from a representative synthetic brine originated from the native brine of the Salar de Hombre Muerto (Argentina) have been investigated. In particular, this paper focuses on the influence of pH, phase volume ratio, chemical structure of the alcohols and the nature of the diluent (kerosene, sulfonated kerosene, and mixture of kerosene and toluene or *m*-xylene) on boron extraction efficiency, stripping efficiency and selectivity.

This study pioneers a comprehensive exploration in boron extraction from high salinity brine by using a synthetic solution mirroring the composition of the brine from the Salar de Hombre Muerto (Argentina). Unlike prior research focused solely on boron extraction without considering co-extraction of other cations, our work delves into the concurrent extraction of various elements within the brine. Furthermore, this work identified efficient and selective solvent extraction systems for boron recovery directly from brine without solar evaporation and paves the way to produce high-grade boric acid or borax, presenting a complementary approach to conventional boron extraction from brines. Our findings also highlight the overlooked aspect of alcohol solubility in brine due to the scarcity of literature data regarding alcohol solubility in brines. Finally, this paper describes the intricate physico-chemistry of boron speciation within the brine, elucidating how pH influences extraction and revealing the concurrent extraction of magnesium and calcium at elevated pH values. Consequently, this work enriches the literature by broadening the understanding of brine processing for boron production.

2. Materials and methods

2.1. Materials

Mono-hydroxy alcohols, i.e. 1-octanol (purity = 99%), 2-butyl-1-octanol (purity = 95%), 2-ethyl-1-hexanol (purity = 99.6%), and di-hydroxy alcohols, i.e. 2-methyl-2,4-pentanediol (purity = 99%), 2-ethyl-1,3-hexanediol (purity = 97%) and 2-butyl-2-ethyl-1,3-propanediol (purity = 99%), were purchased from Sigma-Aldrich (France). Kerosene (Low odor) and *m*-xylene (purity = 99%) were also provided by Sigma-Aldrich (France) while toluene (purity = 100%) was supplied by VWR (France). Sulfonated kerosene (sulfur content = 0.69 mg kg⁻¹) was purchased from Maoming Taihong Petrochemical co., Ltd.

Table 1

Extraction solvents of boron from native brines, synthetic brines and boric acid solution.

Extractants*	Diluents	T (°C)	O/A	EB (%)	pH	Aqueous solution	Ref.
AlICY-IL	Kerosene	23	1	60	8	Synthetic brine	(Fortuny et al., 2012)
Menthol and MPD	–	25	2	83	2	Boric acid	(Almustafa et al., 2020)
Thymol and TMPD	–	25	2	98	2	Boric acid	(Almustafa et al., 2021)
TMPD	Chloroform	25	1	97	2	Xitajiner Salt Lake brine	(Peng et al., 2021)
EHD and CTMP	Petroleum spirit	25	1	95	11	Synthetic brine	(Ayers et al., 1981)
DHD	<i>n</i> -amyl alcohol	25	1	87	12	Boric acid	(Hoşgoren et al., 1997)
BEPD	2-ethyl-1-hexanol	25	1	80	6	Boric acid	(Matsumoto et al., 1997)
TMHD	Kerosene	25	1	95	2	Synthetic brine	(Tural et al., 2007)
EH	Sulfonated kerosene	25	1	99	2.4	Pretreated East Taijinaier Salt lake brine	(Zhang et al., 2016)
TMPD and EH	Sulfonated kerosene	25	1	99.9	1.5	Concentrated Salt Lake brine	(Guo et al., 2020a)
TMhD	Chloroform	25	1	97	2	Synthetic brine	(Karakaplan et al., 2004)
EHD	Sulfonated kerosene	25	0.5	99	2	Concentrated Dahzou underground brine	(Fan et al., 2018)
BOc	Sulfonated kerosene	20	1	99	1	Acidified West Taijinaier Salt Lake brine	(Peng et al., 2018)

(EB: boron extraction efficiency, O/A: organic-aqueous volume phase ratio, T: temperature). *: AlICY-IL=methyltriocetyl/decylammonium bis-(2,4,4(trimethylpentyl)) phosphinate, CTMP2-chloro-4-(1,1,3,3-tetramethylbutyl)-6-methylol-phenyl, MPD = 2-methyl-2,4-pentanediol, TMPD=2,2,4-Trimethyl-1,3-pentanediol, EHD=2-ethyl-1,3-hexanediol, DHD=1,2-dihydroxy-4-oxadodecane, BEPD=2-buty-2-ethyl-1,3-propanediol, TMHD=2,2,6-Trimethyl-1,3-Heptanediol, EH=2-ethyl-1-hexanol, TMhD=2,2,5-trimethyl-1,3-hexanediol, BOc=2-butyl-1-octanol.

Table 2
Structures and dynamic viscosities of the selected alcohols at 35 °C.

Alcohols	Number of carbon atoms in the alkyl chain	Structures	η_1 (mPa s)	η_2 (mPa s)
2-butyl-1-octanol (BOc)	12		18	0.8
2-ethyl-1-hexanol (EH)	8		7.5	0.6
1-octanol (Oc)	8		7.3	0.7
2-ethyl-1,3-hexanediol (EHD)	8		186.5	0.8
2-butyl-2-ethyl-1,3-propanediol (BEPD)	9		Solid	1
2-methyl-2,4-pentanediol (MPD)	6		27.6	0.7

(η_1 =dynamic viscosity of pure alcohol, η_2 =dynamic viscosity of 1 mol L⁻¹ alcohol diluted in kerosene+60% (wt) toluene).

The brine of the Salar de Hombre Muerto (Argentina) contains a large variety of ions including lithium, boron, potassium, magnesium, calcium, sodium, chloride, sulfate, strontium, and iron (Díaz Nieto et al., 2019, 2020). This brine is highly concentrated in monovalent and divalent elements as shown in Table 3. Preliminary experiments showed that under the same extraction conditions, i.e. same concentration of extractant, phase volume ratio, pH and temperature, no significant difference in the extraction efficiency of boron between the native brine and the synthetic brine was observed. Therefore, the extraction properties of the above-mentioned extractants were investigated by using a synthetic solution representative of the brine from the Salar de Hombre Muerto, for which the elemental composition is given in Table 3 (iron and strontium were not accounted for in the synthetic brine as their concentrations were lower than 0.1 g L⁻¹).

The purity and suppliers of reagents were as follows: MgCl₂ (purity = 98%, Sigma-Aldrich), CaCl₂ (purity = 90%, Sigma-Aldrich), H₃BO₃ (Sigma-Aldrich, purity = 99.5%), Li₂SO₄ (Sigma-Aldrich, purity = 98.5%), NaCl (VWR, purity = 99.9%) and KCl (VWR, purity = 99.5%). They were used as received to prepare the synthetic brine by dissolution in deionized water (resistivity = 18 MΩ cm) produced by using Puraniry TU (VWR). The concentrations of the main elements, the pH and the densities of the brine and the synthetic brine are presented in Table 3. Solutions of HCl (purity = 37%, Sigma-Aldrich) and NaOH (purity = 99%, VWR) were used to adjust the pH of the synthetic brine and to strip boron from the loaded organic.

Table 3
Composition, pH and density at room temperature of the brine from the Salar de Hombre Muerto and the synthetic brine.

Brine	pH	Density (g cm ⁻³)	Concentration of ions (g L ⁻¹)									
			Li	Ca	Mg	B	Na	Sr	K	Fe	Cl ⁻	SO ₄ ²⁻
Salar de Hombre Muerto	6.9	1.2	1.27	0.68	3.09	1.62	103.24	0.079	14.21	0.001	182.85	11.15
synthetic brine	5.5	1.2	1.27	0.68	3.09	1.62	103.24	0 ^a	14.21	0 ^a	182.25	8.78

^a Iron and strontium were lower than 0.1 g L⁻¹ and not considered in the synthetic brine

2.2. Methods

2.2.1. Solvent extraction and stripping

Solvent extraction experiments were carried out at 35 °C by mixing 5 mL of the synthetic brine with volumes of organic phases ranging from 5 to 35 mL depending on the phase volume ratio O/A. The organic phases contained 1 mol L⁻¹ alcohols (2-butyl-1-octanol (BOc), 2-ethyl-1-hexanol (EH), 1-octanol (Oc), 2-ethyl-1,3-hexanediol (EHD), 2-methyl-2,4-pentanediol (MPD) or 2-butyl-2-ethyl-1,3-propanediol (BEPD)) diluted in kerosene, sulfonated kerosene or a mixture of kerosene and toluene or *m*-xylene. 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 the extraction, the boron-loaded organic phase was stripped with 5 mL of 0.2 mol L⁻¹ hydrochloric acid, 0.2 mol L⁻¹ sodium hydroxide or deionized water at O/A = 2 and 4, and 35 °C.

Preliminary experiments on the extraction of boron, lithium, potassium, magnesium, calcium and sodium vs. time showed that the equilibria were reached in all cases within 4 h (Figs. S1 and S2 in supporting information (SI) for 1 mol L⁻¹ 2-butyl-1-octanol diluted in kerosene for the sake of illustration) whereas 2 h were needed to strip boron from the organic phases Fig. S3 in SI shows boron stripping from 1 mol L⁻¹ 2-butyl-1-octanol diluted in kerosene for the sake of illustration. Therefore, all extraction and stripping experiments were performed by contacting the organic phases and the aqueous phases during 4 h and 2 h, respectively, at a shaker rate of 200 rpm and a temperature of 35.0 ± 0.2 °C. Extraction and stripping steps were performed with a thermostated shaker (Gherardt Laboshake THL500/1). It is obvious that more

intensive mixing/shaking will make the equilibrium to be reached faster. Afterwards, the biphasic were centrifuged at 3000 rpm for 2 min with a SIGMA 3-16 L centrifuge in order to separate the organic and the aqueous phases. Then, the aqueous and organic droplets were removed from the organic and the aqueous phases, respectively, by filtering with 0.20 μm minisart, made of regenerated cellulose, to filter the aqueous phase and polypropylene to filter the organic phase (Sartorius, France).

2.2.2. Analysis

After the centrifugation and filtering steps, the organic and the aqueous phases were used for different analyses. Exactly 1 mL of the aqueous phase was sampled and diluted in 2% (vol.) nitric acid prepared by diluting concentrated nitric acid (purity = 65%, Sigma-Aldrich) in deionized water. Elemental analyses of the samples were performed with a microwave plasma-atomic emission spectroscopy (MP-AES model 4210, Agilent, France). The results were confirmed by inductively coupled plasma-optical emission spectroscopy (ICP-OES model 7400 Duo, Thermo Fisher Scientific, France). Standards (element concentration = 1000 mg L^{-1}) for elemental analyses of boron, potassium, magnesium, sodium, calcium and lithium were purchased from Sigma-Aldrich. The samples were diluted 100 times for calcium analysis and 1000 times for the analysis of other elements, before MP-AES and/or ICP-OES analysis. It was supposed that chloride and sulfate concentrations in the aqueous phase were stable during the experiments. In order to avoid the well-known matrix effect (Barth, 1997; Chen-ling et al., 2021; Kühn et al., 1998; Tao et al., 2020), the standardization was performed in matrix containing 182 mg L^{-1} chloride and 9 mg L^{-1} sulfate for sodium analysis. Then, after verification, as sodium concentration was rather stable in the extraction samples, boron, potassium, lithium and magnesium were analyzed in a matrix containing 103 mg L^{-1} sodium, 182 mg L^{-1} chloride and 9 mg L^{-1} sulfate. Unlikely, 1032 mg L^{-1} sodium, 1822 mg L^{-1} chloride and 90 mg L^{-1} sulfate constituted the matrix when calcium was analyzed. Chloride, sulfate and sodium concentrations in the matrices were obtained with hydrochloric acid (purity = 37%, Sigma-Aldrich), sulfuric acid (purity = 96%, Sigma-Aldrich) and 26 g L^{-1} sodium chloride, respectively. Before boron, potassium, lithium, magnesium and calcium analyses, sodium, chloride and sulfate concentrations in the stripping samples were adjusted to their contents in the above-mentioned matrices. In the case of MP-AES analysis, 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. In the case of ICP-OES, 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-balance was checked by analyzing the element concentration after full stripping of the organic phase. After analyzing the aqueous phases, the distribution ratio of the element e (D_e), the extraction efficiency of the element (E_e (%)), the selectivity coefficients of the element e_1 towards the element e_2 (S_{e_1/e_2}) and the stripping efficiency of boron (SE_B) were calculated as follows:

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

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

where $C_{e,\text{aq}}$ and $C_{e,\text{org}}$ 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 Eqs. 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 is the phase volume ratio between the organic (O) and the aqueous (A) phases, also denoted as O/A ratio.

The selectivity coefficient for e_1 over 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:

$$SE_B(\%) = \frac{C'_{B,\text{aq}} \times V'_{\text{aq}}}{C'_{B,\text{org}} \times V'_{\text{org}} + C'_{B,\text{aq}} \times V'_{\text{aq}}} \times 100 \quad (5)$$

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

The standard deviation on the extraction and stripping experiments, and the error on the analytical method were estimated to be within 4% by repeating the experiments three times and analyzing the synthetic brine 20 times, respectively.

Dynamic viscosities of the organic phases before and after extraction were determined at 35 °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 analyzed twice. The viscometer cell was cleaned by rinsing with pure ethanol and dried with air after each viscosity measurement. The Stabinger viscometer™ determines the value of the kinetic viscosity (ν) and the density of the samples (ρ). The dynamic viscosity (η) is calculated by multiplying the kinetic viscosity by the density:

$$\eta = \nu \times \rho \quad (6)$$

Water contents in the organic phases after extraction were analyzed by using a volumetric Karl Fisher Titrator (Mettler Toledo, France) after calibration with a standard containing 1% water (Sigma-Aldrich). The total organic carbon in the brine was determined by means of the Shimadzu TOC-VCSH apparatus after contacting the brine with the organic phase (alcohol dissolved in diluent) and with the diluent. The difference between the total organic carbon in the brine contacted with the extractant in diluent and the brine contacted with the diluent alone, under the same experimental conditions corresponds to the total organic carbon in the brine due to the solubility of the alcohol in the brine. Therefore, the solubility of the alcohol in the brine (S_{alc}) can be calculated by using the following equation:

$$S_{alc} = \frac{(TOC_S - TOC_D)}{X} \quad (7)$$

where TOC_S is the Total Organic carbon in the brine after contacting the organic phase composed of the alcohol (extractant) and the diluent, TOC_D is the contribution of the diluent to the Total Organic Carbon in the brine determined by contacting the neat diluent with the brine and X is the carbon mass fraction in the alcohol.

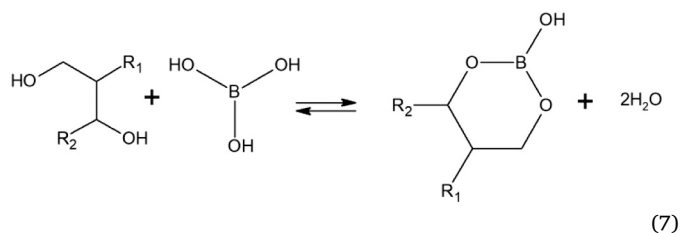
2.2.3. Speciation calculations

Boron speciation is complex and many different species can exist in solution depending on pH and concentrations of boron and other elements in the aqueous solutions (Graff et al., 2017). This speciation can influence (increase or decrease) the extraction efficiency and the selectivity of the extractant. Therefore, speciation calculations of boron in the synthetic brine were calculated on a PC under Windows 11 with the free software Phreeqc ver. 3.7 (Parkhurst and Appelo, 2013) by using

the Pitzer and Minteq.V4 databases. The thermodynamic constants included in the database for speciation calculations are reported in Table S1. The speciation diagrams of boron as a function of pH in pure water as well as boron, calcium, potassium, lithium, magnesium and sodium in the synthetic brine are reported in Figs. S4-S10 of SI.

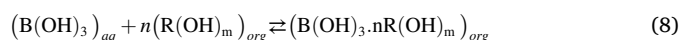
3. Results and discussion

Several authors (Ayers et al., 1981; Bachelier and Verchere, 1995; Grinstead, 1972; Peng et al., 2018; Xu et al., 2021) reported that boric acid is extracted by mono-alcohols or di-hydroxy alcohols from low to high ionic strength aqueous solutions by an esterification reaction. For instance, Fan et al. (2018) mentioned that the extraction of boric acid with 2-ethyl-1,3-hexanediol occurs according to the following esterification reaction:



where R_1 and R_2 are ethyl and propyl groups, respectively.

Conversely, Zhang et al. (2016) assumed that an esterification cannot explain boron extraction by alcohols as the rate of esterification may be too slow during solvent extraction. Therefore, they expected that boron extraction under acidic conditions occurs through the following classical solvation equilibrium already reported in other studies (Guo et al., 2020a; Peng et al., 2018; Lü et al., 2014):



where $\text{R(OH)}_m\text{(org)}$ is the alcohol (mono-alcohol for $m = 1$ and poly-alcohol for $m > 1$) in the organic phase. The subscripts “aq” and “org” mean that the species are in the aqueous phase and the organic phase, respectively.

The following equation derived from the equilibrium (8) shows that the extraction efficiency of boron depends on the temperature, the phase volume ratio O/A and the alcohol concentration in the organic phase at the equilibrium:

$$\log\left(\frac{E_B}{100 - E_B}\right) = \log(K_{ex}(T)) + n \cdot \log([R(OH)_m]) + \text{Log}(O/A) \quad (9)$$

where K_{ex} is the equilibrium constant of Eq. (8) and T is the temperature.

Therefore, the influence of the extractant and the diluent on boron extraction efficiency was studied at constant temperature and for different values of O/A. Although pH does not directly affect the extraction efficiency as shown in Eq. (9), the influence of pH was studied in this paper since the boron speciation depends on pH (Figs. S4, S5, S6 and S9), which can affect boron extraction efficiency.

3.1. Influence of the diluent on boron extraction

Preliminary experiments were carried out to investigate the solubility of the alcohols reported in Table 2 in kerosene, sulfonated kerosene, toluene and *m*-xylene. All mono-hydroxy alcohols and di-hydroxy alcohols are soluble in toluene and *m*-xylene at 1 mol L^{-1} or 2 mol L^{-1} , showing the good solvation of these alcohols by these diluents. Conversely, di-hydroxy alcohols (EHD, MPD and BEPD, see full nomenclature and chemical formulas in Table 2) are not soluble in kerosene or sulfonated kerosene at 1 mol L^{-1} . The much lower solubility of di-hydroxy alcohols may be explained by the tendency of di-hydroxy alcohols to form highly stable dimers, or even species with higher

aggregation number. Aggregation of the alcohol molecules may reduce their solubility in low dielectric solvents such as kerosene and sulfonated kerosene. Finally, it was possible to solubilize 1 mol L^{-1} di-hydroxy alcohols in the mixture of 40% (wt) kerosene and 60% (wt) toluene as well as in the mixture of 40% (wt) kerosene and 60% (wt) *m*-xylene. Therefore, the extraction properties of the alcohols reported in Table 2 were compared in kerosene, sulfonated kerosene and kerosene modified with 60% (wt) toluene or *m*-xylene.

The extraction efficiencies of boron from the synthetic brine by 1 mol L^{-1} alcohol diluted in kerosene, sulfonated kerosene and mixed diluents of kerosene with 60% (wt) toluene or 60% (wt) *m*-xylene are reported in Table 4. There is no significant influence of the diluent on boron extraction when mono-alcohols (BOc, EH and Oc) or di-hydroxy alcohols (EHD, BEPD and MPD) were used as extractants. Likewise, the addition of toluene or *m*-xylene in the diluent does not significantly influence the water solubility in the extractant. Table 4 shows that alcohols diluted in mixtures of kerosene and toluene or kerosene and *m*-xylene exhibit the lowest viscosities. The viscosity values remain the same before and after boron extraction indicating that the extracted boron does not influence the viscosity of the organic solvents.

3.2. Influence of the extractant on boron extraction

Fig. 1 shows the influence of O/A volume ratio on the extraction efficiency of boron by the different extractants diluted in kerosene (Fig. 1a) or a mixture of kerosene and 60% (wt) toluene (Fig. 1b). The boron extraction efficiencies by mono-alcohols in kerosene follow the same order (i.e., $\text{BOc} \sim \text{EH} > \text{Oc}$) which was not significantly affected by the O/A volume ratio (Fig. 1a). In contrast, only a slight influence of O/A volume ratio on boron extraction efficiencies was observed when the di-hydroxy alcohols were used as the extractant. The extraction efficiencies decrease slightly, especially for low values of O/A volume ratios, according to the following order: $\text{EHD} > \text{BEPD} > \text{MPD}$ (Fig. 1b).

Regarding the mono-hydroxy alcohols, the highest extraction efficiency of BOc may be attributed to the highest hydrophobicity as the number of carbon atoms in BOc (12 carbon atoms) is greater than in Oc (8 carbon atoms). Among the mono-hydroxy alcohols, EH exhibits a higher extraction efficiency than Oc despite the same number of carbon atoms, likely because of the presence of ramifications in the chemical structure of EH, which may contribute to a higher stability of the extracted complex.

The DFT calculations showed that the two hydroxyl groups in 1,3-di-hydroxy alcohols may stabilize boron in the organic phase by forming a six-member ring species (Garrett, 2004d,a; Guo et al., 2020b; Peng et al., 2021). Therefore, the presence of two hydroxyl groups in di-hydroxy alcohols increase the extraction efficiency since similar complexes and stabilization are expected with MPD, EHD and BEPD. The difference in boron extraction efficiency for this class of molecules is not significant and within the experimental error as 99%, 97.4% and 96.4% boron were extracted by EHD, BEPD and MPD at O/A volume ratio of 2, respectively (Fig. 1b).

3.3. Influence of the pH on boron extraction

The extraction properties of the alcohols were studied as a function of pH at a constant phase ratio $O/A = 2$ in the mixed diluent of kerosene and toluene and at $O/A = 4$ in kerosene so that the extraction efficiencies is high enough to test the influence of pH on extraction efficiency ($>30\%$). Fig. 2 shows that the same trend is observed irrespective of the nature of the alcohols. The boron extraction efficiency is constant until $\text{pH} \sim 5.5$. Above this pH, the extraction efficiency decreases sharply depending on the nature of the alcohol. The values of the boron extraction efficiency in the plateau region ($\text{pH} < 5.5$) depends on the nature of the extractant and follows the order: $\text{BOc} \sim \text{EH} > \text{Oc}$, when the alcohol is diluted in kerosene, and $\text{EHD} > \text{BEPD} > \text{MPD}$ when the alcohol is diluted in kerosene modified with toluene.

Table 4

Effect of diluents on boron extraction efficiency (E_B), dynamic viscosity (η) and water solubility in the organic phase (w_{H_2O}) after boron extraction by the extractant 1 mol L⁻¹ alcohol.

Alcohol	Diluents											
	Kerosene			Sulfonated kerosene			Kerosene and 60% (wt) toluene			Kerosene and 60% (wt) <i>m</i> -xylene		
	E_B (%)	η (mPa s)	w_{H_2O} (%wt)	E_B (%)	η (mPa s)	w_{H_2O} (%wt)	E_B (%)	η (mPa s)	w_{H_2O} (%wt)	E_B (%)	η (mPa s)	w_{H_2O} (%wt)
BOc	22.2	2	0.1	23.5	1.7	0.1	22.2	0.8	0.2	21.7	0.9	0.1
EH	23.4	1.6	0.1	17.4	1.3	0.1	17.4	0.6	0.2	22.1	0.7	0.2
Oc	10.4	1.7	0.2	9.4	1.4	0.2	9.9	0.7	0.3	14.0	0.7	0.2
EHD	ns	ns	ns	ns	ns	ns	97.2	0.8	0.6	96.2	0.9	0.6
BEPD	ns	ns	ns	ns	ns	ns	93.7	1	0.7	93.6	1.1	0.7
MPD	ns	ns	ns	ns	ns	ns	89.7	0.7	0.7	88.8	0.7	0.6

(O/A = 1, pH = 1, 35 °C, ns: not soluble, i.e. solubility < 1 mol L⁻¹).

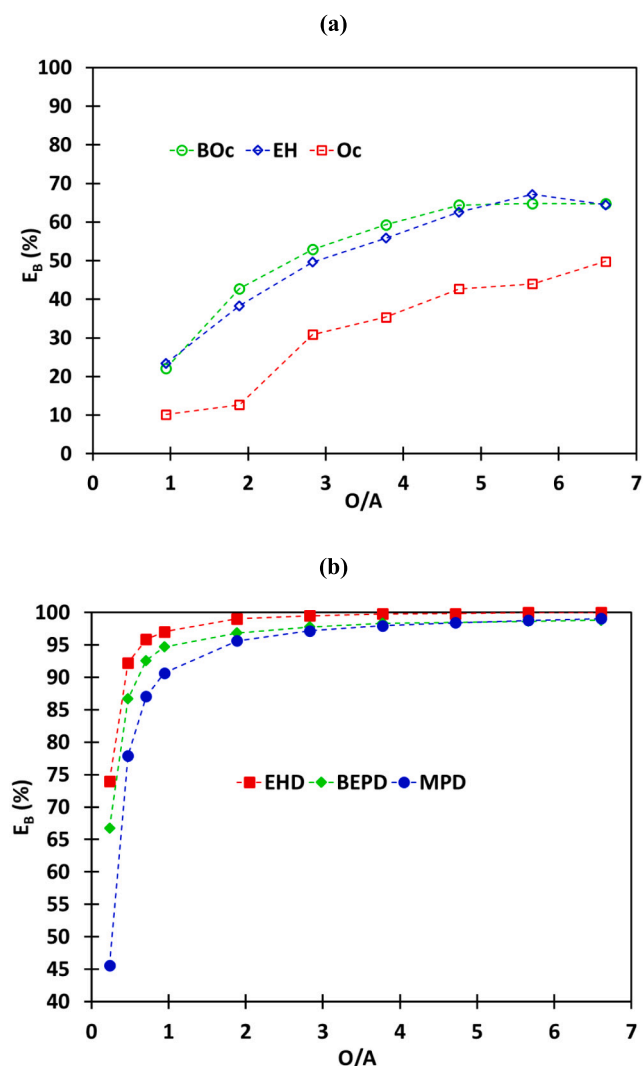


Fig. 1. Influence of O/A volume ratio on the extraction efficiencies of boron by 1 mol L⁻¹ (a) mono-hydroxy alcohols diluted in kerosene and (b) di-hydroxy alcohols diluted in kerosene modified with 60% (wt) toluene at pH = 1 and 35 °C.

According to Eq. (8), the extraction efficiency of boron should not depend on the pH in the aqueous phase. However, Fig. 2a shows a significant decrease in extraction efficiency of boron by mono-hydroxy alcohols when the pH of the aqueous phase is >5.5. This phenomenon may be explained by (i) change in boron speciation, (ii) co-extraction of other elements or (iii) salting-out effect. There is no salting-out effect as the ionic strength in the aqueous solutions does not change significantly

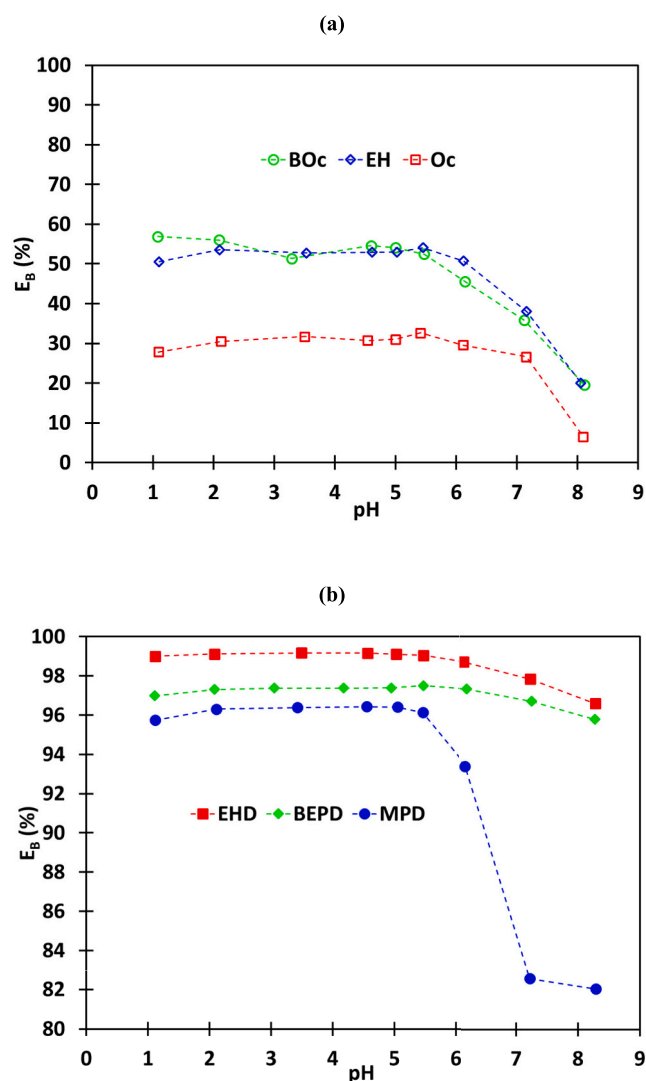


Fig. 2. Influence of the initial pH on boron extraction from the synthetic brine by (a) the mono-hydroxy alcohols BOc, EH and Oc diluted in kerosene (O/A = 4) and (b) the di-hydroxy alcohols EHD, BEPD and MPD diluted in kerosene modified with 60% (wt) toluene (O/A = 2). Alcohol concentration = 1 mol L⁻¹; 35 °C. No co-extraction of K, Li, Mg, Ca and Na was observed with mono-hydroxy alcohols.

according to Phreeqc calculations ($I = 3.5\text{--}3.6 \text{ mol kg}^{-1}$). Likewise, the drop in extraction efficiency cannot be explained by co-extraction of impurities as no co-extraction of other elements occurs at pH >5.5 when mono-hydroxy alcohols are used as extractant. Therefore, the decrease

of boron extraction efficiency can be explained by the decrease in concentration of the extractable boron species, i.e. H_3BO_3 , when pH is >5.5 (Fig. 3), the formation of non-extractable anionic species of boron ($\text{B}(\text{OH})_4^-$, $\text{H}_5(\text{BO}_3)_2$, $\text{B}_3\text{O}_3(\text{OH})_4^-$, H_2BO_3^- , $\text{H}_8(\text{BO}_3)_3^-$ and $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$) and the formation of the non-extractable mixed complexes (ion-pairs) NaH_2BO_3 , $\text{MgH}_2\text{BO}_3^+$, $\text{CaH}_2\text{BO}_3^+$, $\text{CaH}_2\text{B}(\text{OH})_4^+$ and $\text{MgH}_2\text{B}(\text{OH})_4^+$ (Fig. S5 in the SI). The non-extractability of these mixed complexes by the mono-hydroxy alcohols is supported by the absence of sodium, magnesium and calcium co-extraction along with boron.

Conversely, calcium and magnesium are coextracted at pH >6 whereas no co-extraction of sodium, potassium and lithium occurs when di-hydroxy-alcohols are used instead of mono-hydroxy alcohols (Fig. 4). Therefore, the mixed complex NaH_2BO_3 is not significantly extractable by di-hydroxy-alcohols while mono-hydroxy-alcohols can extract it more efficiently. It is also of interest to point out that the drop of boron extraction efficiency at pH >5.5 is much less pronounced in the case of di-hydroxy-alcohols than mono-hydroxy alcohols. This is attributed to the decrease in concentration of the extractable species, H_3BO_3 , which is compensated by the formation of $\text{CaH}_2\text{BO}_3^+$ and $\text{MgH}_2\text{BO}_3^+$ (Fig. 3) that may be extracted by forming a neutral extractable species with chloride anions, i.e. $\text{CaH}_2\text{BO}_3\text{Cl}$ and $\text{MgH}_2\text{BO}_3\text{Cl}$. The extraction of these mixed species in the organic phase is supported by the drop of selectivity towards calcium and magnesium depicted in Fig. 4 at pH >6 , where calcium and magnesium are co-extracted with boron at alkaline pH by di-hydroxy alcohols while no co-extraction occurs when mono-hydroxy alcohols are used as extractant.

Fig. 3 shows that calcium is the main species co-extracted at pH 8.3 by both BEPD and EHD with a selectivity ($S_{\text{B}/\text{Ca}}$) of 16.5 and 41.3, respectively, for boron over calcium. At pH 8.3, MPD exhibits a high selectivity of boron over magnesium ($S_{\text{B}/\text{Mg}} = 21.2$). Hydrophobicity, branching at the vicinity of the hydroxyl functional group of the aliphatic alcohols and the number of hydroxyl groups influence the extraction efficiency and the selectivity.

Figs. 2 and 4 show that the highest extraction efficiency and selectivity of boron from the synthetic brine is obtained at pH 5.5 when 1 mol L^{-1} BOC, EH or Oc is diluted in kerosene ($O/A = 4$) or 1 mol L^{-1} EHD, BEPD or MPD is diluted in the mixture of kerosene and toluene ($O/A = 2$). Furthermore, boron extraction at pH 5.5 reduces any requirement for pH adjustment of the brine.

Table 5 reports the extraction efficiencies of boron by the alcohols under the optimal extraction conditions, the dynamic viscosity of the organic phases after extraction, the water solubility in the organic phases and the solubility of the alcohols in the brine deduced from the measurements of total organic carbon (TOC).

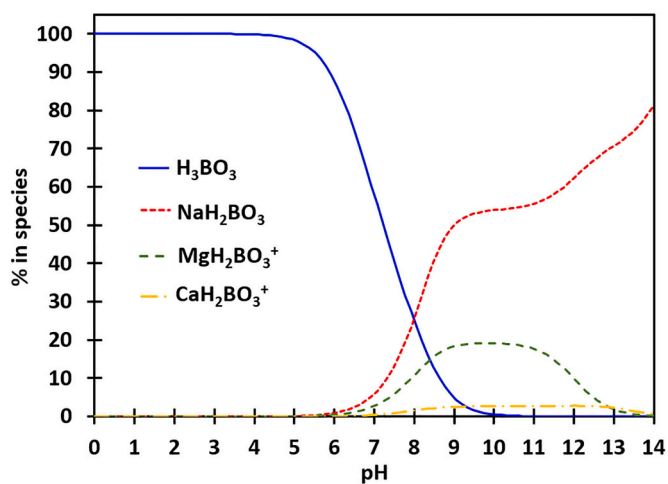


Fig. 3. Boron speciation in the synthetic brine as a function of initial pH (only the extractable boron species and the non-extractable species NaH_2BO_3 are reported).

The water solubility in the organic phases is higher with di-hydroxy alcohols ($\sim 0.7\%$) than with mono-hydroxy alcohols ($\sim 0.2\%$) (Table 5). Therefore, the presence of two hydroxyl groups in the alcohol molecules favors water extraction to the organic phases. Conversely, they promote the boron extraction and exhibit higher extraction efficiency than mono-hydroxy alcohols. However, the presence of two hydroxyl groups increases the hydrophilicity of the molecules, and therefore, increase the solubility of di-hydroxy alcohols in the brine as shown by the higher values of S_{alc} in Table 5. The hydrophilicity decreases when the number of carbon atoms in the alkyl chains of the alcohols increase as shown in Table 5. Indeed, the solubility of mono-hydroxy alcohols in the brine ($S_{\text{alc}} = 19\text{--}43 \text{ mg L}^{-1}$) are significantly below those reported by Garrett and Folkestad who acknowledged solubilities of not $<200 \text{ mg L}^{-1}$ for equivolume mixture of kerosene and isooctanol (Garrett, 2004b; Folkestad et al., 1974). However, the solubility of BEPD (259 mg L^{-1}) in the synthetic brine was greater than that of isooctanol diluted in kerosene (200 mg L^{-1}). For all alcohols (mono-hydroxy alcohols and for di-hydroxy alcohols) investigated, the solubility in the synthetic brine follows the following order reflecting the effect of the number of carbon atoms in the alkyl chain (Table 2): BOC (12 carbon atoms) $<$ EH (8 carbon atoms) $<$ Oc (8 carbon atoms); and BEPD (9 carbon atoms) $<$ $<$ EHD (8 carbon atoms) $<$ $<$ MPD (6 carbon atoms).

The increase of the number of carbon atoms in the alkyl chains is responsible for an increase of the hydrophobicity. When the number of carbon atoms in the alkyl chains and hence the hydrophobicity of the molecule increases, the extraction efficiency also increases. Indeed, in the case of linear mono-hydroxy alcohols, the extraction efficiency of boron increases from 32% to 55% when the number of carbon atoms in the alkyl chains increases from 8 for Oc to 12 for BOC. There is no significant difference in hydrophobicity between Oc and EH as they have the same number of carbon atoms in the alkyl chains. However, the extraction efficiency of boron by EH is greater than by Oc. Therefore, it seems that ramification (branching) of the alkyl chains increases the extraction efficiency of boron. The ramification favors the extraction of boron by stabilizing the boric acid in the complex formed between boric acid and alcohol. Conversely, it is difficult to conclude for di-hydroxy alcohols since there is no significant difference of the boron extraction efficiencies as a function of the ramification and the number of carbon atoms in the alkyl chains.

3.4. Boron stripping

Several authors reported that hydrochloric acid (HCl), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4) and deionized water can be used to strip boron (Hoşgoren et al., 1997; Kumar et al., 2015; Zhang et al., 2016). In this study, stripping tests of boron contained in the loaded organic phases were performed with 0.2 mol L^{-1} hydrochloric acid, 0.2 mol L^{-1} sodium hydroxide, and deionized water (Figs. 5).

Fig. 5 shows that the stripping efficiency of boron is greater in the presence of mono-hydroxy alcohols than that in the presence of di-hydroxy alcohols. This is a result of the stronger interactions between boron and di-hydroxy alcohols compared with that of mono-hydroxy alcohols, as reflected by the higher extraction efficiency of di-hydroxy alcohols than that with mono-hydroxy alcohols. Sodium hydroxide is the best stripping reagent irrespective of the extractants, since alkaline solution favors the formation of $\text{B}(\text{OH})_4^-$, which is not an extractable species (Peng et al., 2021). Likewise, the stripping efficiency with hydrochloric acid is low as acidic reagent like HCl favors the formation of H_3BO_3 , which is highly extractable, and therefore remains in the organic phase. However, the stripping efficiency is not nil when HCl is used probably because of the affinity between boric acid and water molecules, which destabilized boron-alcohol interactions. Xu et al. (2021) (Xu et al., 2021) reported that increasing the concentration of HCl from 0.5 mol L^{-1} to 3 mol L^{-1} reduces the stripping efficiency by about 12%. This is probably due to the high salting-out effect. Indeed, the high salting-out effect is caused by the reduction of water activity and a

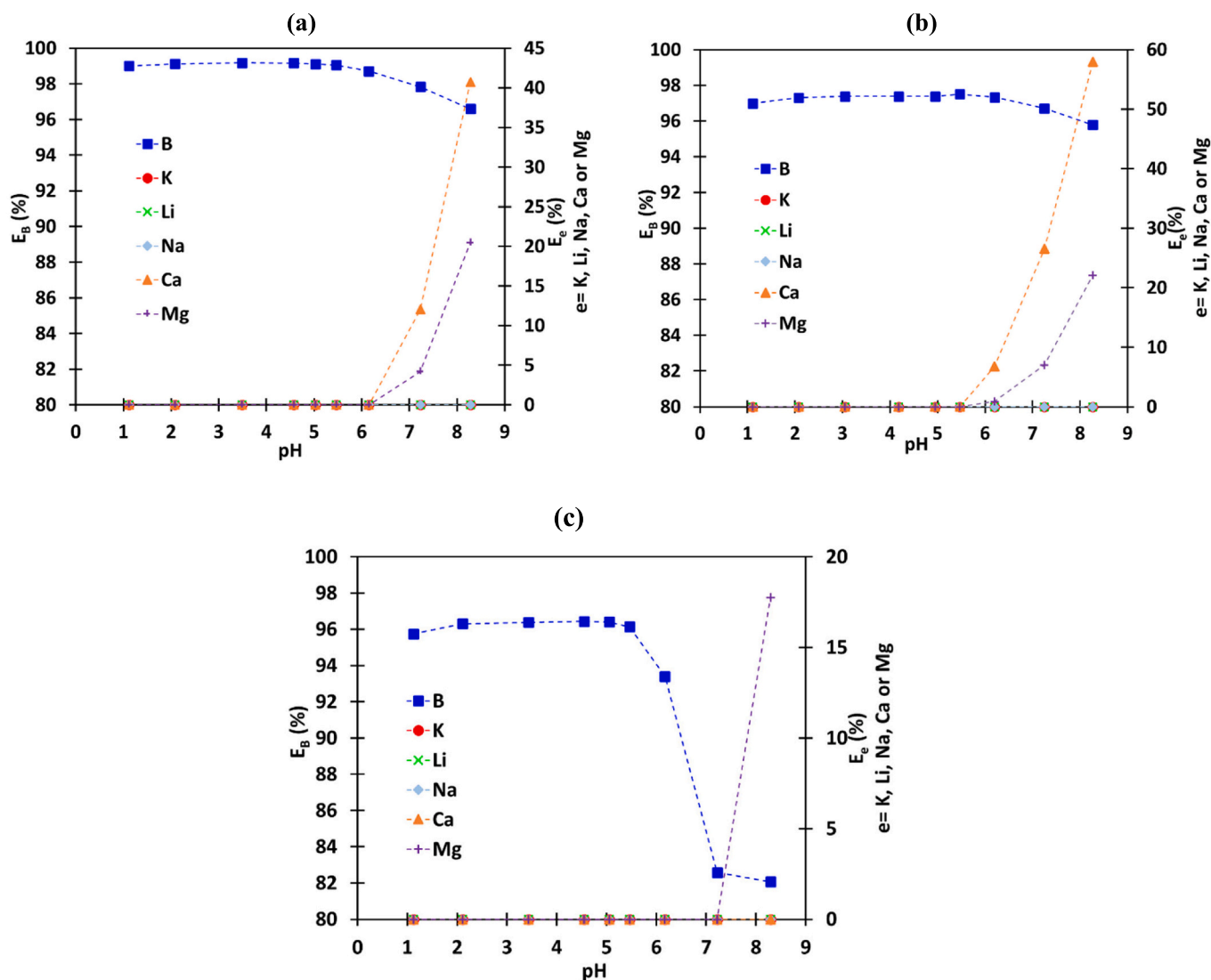


Fig. 4. Influence of the initial pH of brine on the extraction of boron and other elements (K, Li, Mg, Ca and Na) by (a) EHD, (b) BEPD and (c) MPD diluted in kerosene modified with toluene ([alcohol] = 1 mol L⁻¹, O/A = 2, 35 °C).

Table 5

Effect of the two diluents, i.e. kerosene and 60% (wt) toluene, on boron extraction efficiency (E_B), dynamic viscosity (η) and solubility of water (w_{H_2O}) in the loaded organic phase and solubility of the alcohols (S_{alc}) in the synthetic brine.

Monohydroxy alcohols	Kerosene				Dihydroxy alcohols	Kerosene +60% (wt) toluene			
	E_B (%)	η (mPa s)	w_{H_2O} (% wt)	S_{alc} (mg L ⁻¹)		E_B (%)	η (mPa s)	w_{H_2O} (% wt)	S_{alc} (mg L ⁻¹)
BOc	55	2	0.1	19	EHD	99	0.8	0.6	1368
EH	55	1.6	0.2	40	BEPD	97	1	0.7	259
Oc	32	1.7	0.2	43	MPD	96	0.7	0.7	12,603

(O/A = 2 and 4 for alcohols diluted in kerosene and toluene mixture and kerosene, respectively, pH = 5.5, temperature = 35 °C, [alcohol] = 1 mol L⁻¹).

decrease of the affinity between boric acid and water molecules.

It is of interest to point out that deionized water can strip boron even if the stripping efficiency is not high, especially in the systems where dihydroxy alcohols are used as extractants. Therefore, water may destabilize the boron species in the organic phase indicating that the hydrogen bonds between boric acid and water molecules may be stronger than interaction between boric acid and alcohol molecules.

3.5. Potential application

The concomitant recovery of lithium salts and boron compounds is currently in practice at two industrial facilities. In said industrial plants, before boron recovery, the brine is concentrated by solar evaporation and acidified to pH = 2. This practice is currently in place only in the two facilities at Atacama, Chile. Interestingly, the Atacama brine is the one with the highest known lithium concentration (about 1500 mg L⁻¹, and higher in some wells), and where also the highest lithium concentration is reached in the solar ponds (about 60,000 mg L⁻¹ Lithium). Because of

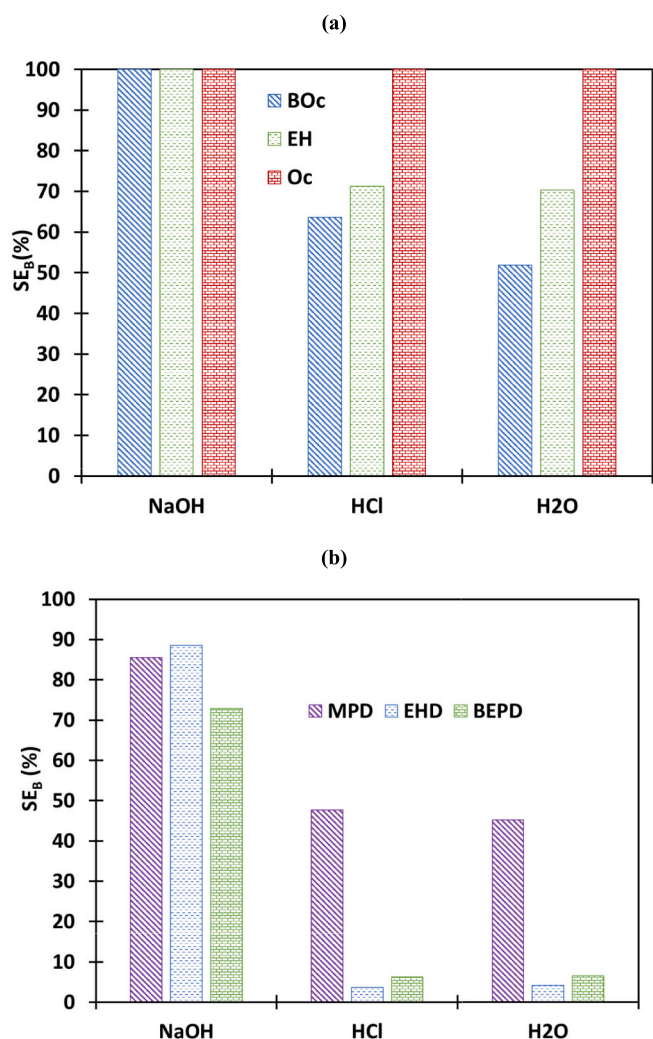


Fig. 5. Boron stripping from an organic phase composed of 1 mol L⁻¹ of (a) mono-hydroxy alcohols in kerosene and (b) dihydroxy alcohols in mixture of kerosene and 60% (wt.) toluene. Stripping solutions: 0.2 mol L⁻¹ NaOH, 0.2 mol L⁻¹ HCl or deionized water; temperature: 35 °C. The loaded organic phase was obtained by contacting the synthetic brine with the fresh organic phase at (a) O/A = 4 and (b) O/A = 2.

the extremely high lithium concentration in the brine after the ponds, the solution volume to be processed for production of 1 ton of lithium carbonate is much lower than at any other brines at competing locations. Hence, it is possible to produce brine after acidification to pH = 2.

Conversely, it is important to recall that this study was performed on an aqueous solution mimicking the composition of a native brine with lithium concentration of 1270 mg L⁻¹ (Table 3). Thus, if we wish to remove boron from this native brine, the volume of brine that needs to be processed to produce 1 ton of lithium carbonate is 47 times higher than the volume of the brine after solar evaporation in Atacama (calculation made assuming 100% lithium recovery efficiency from the brine containing 60,000 mg L⁻¹ lithium). Therefore, the amount of HCl that would be needed to acidify the native brine to pH = 2 would be 47 times greater than in the Atacama case, and very likely infeasible. These numbers put in perspective the importance of finding extractants that can work at either neutral pH or pH values which are closer to those of native brines like those identified in the present work (mono-hydroxy alcohols can be successful at pH around 7 without impurities coextraction).

Moreover, boron removal is key if either magnesium or calcium products wish to be concomitantly recovered. Similarly, to the brine of

Hombre Muerto, all continental brines are rich in both magnesium and calcium cations (Table 3). However, it is largely known that mixed species can be formed from those two cations and boron compounds as shown in Fig. 3. Díaz Nieto et al. (2022) and Bonin et al. (2021) have shown that production of Mg(OH)₂ in pure form from these types of complex brines is only possible if boron is previously removed.

4. Conclusions

Solvent extraction of boron from brines, concentrated by evaporation, has been widely reported in the literature. However, only a few papers address the effect of diluents on boron extraction and selectivity as well as the high alcohol solubility in highly concentrated brines. In this study, liquid-liquid extraction of boron from synthetic brine, closely mimicking the composition of the native brine of the salar de Hombre Muerto, was systematically performed as a function of pH and the phase volume ratio O/A with aliphatic alcohols, i.e. mono-hydroxy alcohols and di-hydroxy alcohols diluted in kerosene and a mixture of kerosene 40% (wt) and toluene 60% (wt). Boron speciation in brine determined by using the Pheeqc software, combined with data on boron extraction, revealed that boron was extracted by all aliphatic alcohols as boric acid at acidic pH, without co-extraction of the other elements (potassium, calcium, sodium, lithium and magnesium). However, at alkaline pH, other cations, such as magnesium and calcium were extracted to the organic phase containing di-hydroxy alcohols due to the decrease of boric acid content and the formation of ion-pairs of borate with these metal ions in the aqueous phase. Due to the two hydroxyl functions, di-hydroxy alcohols were better extractants than mono-hydroxy alcohols, although the extraction should be conducted at acidic pH in order to ensure highest selectivity.

Among the alcohols diluted in kerosene, the 2-butyl-1-octanol containing 12 carbon atoms and the 2-ethyl-1-hexanol containing 8 carbon atoms exhibit the best extraction efficiency of boron (55%) followed by 1-octanol (8 carbon atoms) at 1 mol L⁻¹, O/A = 4, pH = 5.5 and 35 °C. Then, the hydrophobicity and the branching of the alcohol strongly impact the extraction efficiency. The water solubility in the organic phase and the solubility of the alcohols were promoted by di-hydroxy alcohols and alcohols containing low carbon atoms. Among all the aliphatic alcohols investigated, the best extraction efficiency of 99% was found with 1 mol L⁻¹ 2-ethyl-1,3-hexanediol diluted in the mixture of kerosene 40% (wt) and toluene 60% (wt) at pH = 5.5, O/A = 2 and 35 °C. Then, boron was stripped from the organic phase with 88.5% stripping efficiency by 0.2 mol L⁻¹ NaOH at O/A = 2 and 35 °C. These results demonstrate the potential use of 2-butyl-1-octanol and 2-ethyl-1,3-hexanediol for selectively extracting boron from continental native brines. However, 2-butyl-1-octanol was preferred due to its solubility in non-aromatic diluents and its lower solubility in brine compared to 2-ethyl-1,3-hexanediol.

CRedit authorship contribution statement

Abdoul Fattah Kiemde: Writing – original draft, Investigation, Data curation. **Jérôme Marin:** Methodology. **Victoria Flexer:** Writing – review & editing. **Alexandre Chagnes:** Writing – review & editing, Writing – original draft, Validation, Supervision, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.hydromet.2024.106280>.

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