Article

Solvent Extraction of Boric Acid: Comparison of Five Different Monohydric Alcohols and Equilibrium Modeling with Numerical Methods

Adam Balinski *, Volker Recksiek and Norman Kelly

Abstract: Solvent extraction is one of the common methods for the recovery of boric acid (or boron) from aqueous solutions. A wide variety of different compounds including monohydric alcohols has been tested, and there is wide recognition that they are rather ineffective compared to other extractants such as diols. Nevertheless, monohydric alcohols find application in industrial processes, demonstrating their efficiency. The intention of this study is to clarify this discrepancy and to provide an overall picture of monohydric alcohols as an extractant for boric acid. Five different monohydric alcohols are the object of this study: n-octanol, 2-ethyl-1-hexanol, 2-butyl-1-octanol, 2-octanol and 3,7-dimethyl-3-octanol. A special focus of this work is the examination of the effect of the structure of the carbon chain and the effect of the composition of the aqueous phase on the extraction efficiency. As well as the extraction efficiency for boric acid, other important properties are examined such as the viscosity of the organic phase, the solubility of alcohols in the aqueous phase and the co-extraction of salts used as a salting-out agent (NaCl, Na2SO4, MgCl2, LiCl, LiNO3). Finally, a numerical algorithm is developed to calculate the relationship between the number of theoretical stages and the phase ratio at equilibrium for selected extraction systems.

Keywords: boron; boric acid; solvent extraction; separation; monohydric alcohols; n-octanol; 2-ethyl-1-hexanol; 2-butyl-1-octanol; 2-octanol; 3,7-dimethyl-3-octanol; salting-out agent

1. Introduction

Boric acid is produced industrially from borate minerals and brines [1]. The majority of boric acid is obtained from minerals such as borax (Na2[B4O5(OH)4]·8H2O), kerinite (Na2B4O6(OH)2·3H2O) colemanite (Ca[B3O4(OH)3]·H2O) and howlite (Ca2B2O5(SiO4)(OH)3). Borax became by far the most important mineral for the borate industry by the end of the 20th century [2]. As a rule, the production process from high-grade borax concentrates or other alkali borates consists of dissolving borates in mineral or organic acids (HX) (Equation (1)) and the subsequent crystallization of boric acid and sodium salt (NaX) as a by-product. Generally, in the process, sulfuric acid is preferred [3]; however, techniques based on nitric acid [4], oxalic acid [5] and propionic acid [6] have been described.

Na2[B4O5(OH)4]·8H2O + 2HX → 4H3BO3 + 2NaX + 5H2O

(1)

Likewise, the production of boric acid from minerals containing calcium (e.g., colemanite, howlite) uses predominantly acid technology with H2SO4 [7] (Equation (2)).

Ca[B3O4(OH)3]·H2O + H2SO4 + 3H2O → 3H3BO3 + CaSO4·2H2O

(2)

In addition, a process with propionic acid and/or calcium propionate [7], a process with a mixture of sulfuric and propionic acid [8] and a range of patented approaches [9] have been described. The patented approaches, which are reviewed in [9], are applicable
only for mineral concentrates with a low impurity content. The processing of the low-grade mineral concentrates requires additional purification operations such as sulfide precipitation (e.g., for iron and arsenic), alum precipitation (for aluminium) [9] or ion exchange (for magnesium) [8]. Other options for the reduction of the amount of impurities in the mother liquor are (i) the application of weak acids (or acid mixtures) in the process to avoid the decomposition of side minerals, (ii) the discharge of some of the contaminated process liquor to decrease the concentration of impurities and (iii) the slow addition of the acid during the decomposition in order to avoid a high acid concentration at the beginning of the process [8].

Aside from the acid technology, high-purity boric acid (>99.9%) and NaOH as a by-product have been produced by the membrane electrolysis of aqueous borax pentahydrate solution [10–12]. This technique requires a high-purity borax solution as a feed because the performance and life of the membrane are related to the purity of the electrolyte solution [12]. Consequently, the method is currently not suitable for complex low-grade raw materials.

Another important source for boric acid is natural brines. The production of boric acid from these sources is achieved directly or via a borate-intermediate stage (e.g., borate adsorption by addition of Ca(OH)₂ [13]). The preferred method depends on the concentration of boric acid, on the brine composition and on the targeted separation yield. The technological details of the process are usually not revealed by exploiting companies [14]. Apart from the production of boric acid from brines, boron has to be removed by lithium carbonate production from these sources in order to obtain a product of an appropriate purity [15]. The direct production of boric acid is carried out by the crystallization of boric acid [16] or by solvent extraction [17–22], even though ion exchanging systems have also been described in the literature [23,24]. Common anion exchangers are not suitable for the separation of boric acid (more precisely, borate ions) from highly saline solutions. Nevertheless, chelating resins with two hydroxy groups in the cis position, such as WOFATIT MK 51 (Chemie AG, Bitterfeld-Wolfen, Germany), offers a high selectivity towards boron [23,24].

The first step in the boric acid crystallization technique is the acidification of brine—e.g., with hydrochloric acid [16]—in order to convert the borate minerals into boric acid. The solubility of boric acid in aqueous solution is 4.65 g per 100 g of saturated solution, and it decreases with decreasing temperature [25]. Thus, the subsequent precipitation of boric acid from the aqueous solution can be achieved either by cooling or by evaporative concentration. In general, this technique is suitable for brines with a high boron concentration.

If the separation process includes a solvent extraction step, boron compounds can be extracted using different extractants such as monohydric alcohols [21,22,26], aliphatic diols [17,19,27,28], aromatic compounds [18,27,29] or mixed alcohols [20]. According to Brown and Sanderson (1980) [3], boron can be extracted as neutral ester (B(OR)₃), as boric acid complexes (H₂BO₃·ROHₙ) or as tetrahydroxy borate (R⁺B(OH)₄⁻). In addition, the authors state that the extraction of boric acid by monohydric alcohols is caused by purely physical actions and the amount of extracted boric acid is roughly proportional to the concentration of an extractant.

Apart from in the direct production of boric acid, the solvent extraction method has been applied for the purification of brines in lithium production [30], for the recovery of boron from wastewater generated by the LCD manufacturing industry [28], for the recovery of boron from coal fly ash [31] and for reducing boron concentrations in the wastewater from a boron mine [32].

This study investigates the solvent extraction of boric acid with monohydric alcohols in detail. Our motivation was to critically assess the statements of some authors that diols are considered to be the most effective extractants of boric acid [3,19,28]. Nevertheless, the application of monohydric alcohols in the industry [33] demonstrates their high efficiency. The existing studies dealing with the solvent extraction of boric acid with monohydric alcohols [21,22] are limited to certain systems and they do not give a general view of
their strengths and weaknesses. Furthermore, an objective justification for their selection is missing. In this work, the extraction efficiency of the following monohydric alcohols with different steric hindrances illustrated in Figure 1 is assessed: n-octanol, 2-ethyl-1-hexanol, 2-butyl-1-octanol, 2-octanol and 3,7-dimethyl-3-octanol. Furthermore, the effect of the ionic strength on the extraction efficiency using different salts (NaCl, Na₂SO₄, MgCl₂, LiNO₃ and LiCl), the co-extraction of a salting-out agent, the viscosity of the organic phase and the solubility of monohydric alcohols in the aqueous phase are discussed in more detail. Finally, the equilibrium modeling with MATLAB for certain systems is carried out to determine the relationship between the number of theoretical extraction stages and the phase ratio.

![Figure 1. Structural formulas of extractants tested in this study.](image)

2. Materials and Methods

2.1. Extraction and Stripping Experiments

All extraction and stripping experiments were carried out by mixing an organic and an aqueous phase in 5 mL centrifuge tubes at a certain phase ratio (PR) calculated with Equation (3) and by shaking in an overhead shaker.

$$PR = \frac{V_{OP}}{V_{AP}}$$  (3)

The parameters for all conducted extraction and stripping experiments are listed in Table 1. After the phase separation, the concentration of sulfur in the aqueous phase was determined by inductively coupled plasma optical emission spectrometry (ICP-OES; Thermo Scientific IRIS Intrepid II XDL, Basel, Switzerland) and the concentration of sodium, lithium and magnesium was determined by atomic absorption spectroscopy (AAS; Analyik Jena contrAA 700, Jena, Germany). The boron content in the aqueous phase was determined by a colorimetric method using azomethine-H as a complexing agent. The procedure is described in the next section. Additionally, the viscosity of selected mixtures of monohydric alcohols and kerosene was measured (Anton Paar SVM 2001, Ostfildern, Germany).

2.2. Determination of Boric Acid Concentration in Aqueous Solutions

The concentration of boric acid in aqueous solutions was determined by the azomethine-H method described by John et al. (1975) [34]. For this purpose, 2 mL of blank or diluted aqueous solution containing boric acid was pipetted into a 15 mL tube and 4 mL of buffer masking solution were added. After shaking, 4 mL of azomethine-H reagent was added. The reaction mixture was again shaken, and after 60 min the absorbance was measured at 420 nm against a blank (SPECORD 210 PLUS; Analytik Jena AG, Jena, Germany). The azomethine-H solution was prepared by dissolving 0.45 g of azomethine-H monosodium salt hydrate (C₁₇H₁₂NNaO₈S₂·xH₂O; VWR Chemicals, Radnor, PA, USA) and 1 g of L(+)ascorbic acid solution (C₆H₈O₆; Bernd Kraft, Duisburg, Germany) in 100 mL.
of deionized water. The reagent was prepared fresh every day. Buffer masking solution was prepared by dissolving 250 g of ammonium acetate \( (\text{H}_3\text{CCOONH}_4; \text{Merck, Darmstadt, Germany}) \) and 15 g of EDTA disodium salt dihydrate \( (\text{C}_{14}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8\cdot2\text{H}_2\text{O}; \text{Merck, Darmstadt, Germany}) \) in 400 mL of deionized distilled water and slowly adding 125 mL of glacial acetic acid \( (\text{H}_3\text{CCOOH}; \text{Merck, Darmstadt, Germany}) \). The calibration curve was constructed by diluting a boron standard solution \( (1000 \text{ mg/L}; \text{LGC Standards, Wesel, Germany}) \) in a concentration range between 1 and 5 mg/L.

Table 1. Experimental conditions for extraction experiments: (1) effect of alcohol \( (\text{ROH}) \) concentration on distribution ratio, (2) effect on ionic strength on distribution ratio, (3) co-extraction of salting-out agent, (4) determination of equilibrium relationship.

| Experiment | (1) | (2) | (3) | (4) |
|------------|-----|-----|-----|-----|
| \( \text{H}_3\text{BO}_3 \) in aqueous phase [mmol/L] | 185 | 185 | -(deionized water) | case 1: 46, 185, 738 case 2: 185 |
| Organic phase (vol% of extractant diluted in kerosene) | n-octanol | 2-ethyl-1-hexanol | Loaded organic phases from experiment (2) | 2-ethyl-1-hexanol |
| | (10–100) | (70) | | (70) |
| | 2-ethyl-1-hexanol | 2-octanol | | |
| | (10–100) | (70) | | |
| | 2-butyl-1-octanol | 2-butyl-1-octanol | | |
| | (10–100) | (70) | | |
| | 2-octanol | | | |
| | (10-100) | | | |
| | 3,7-dimethyl-3-octanol | | | |
| | (10-100) | | | |
| Phase ratio [-] | 2 | 2 | 1 | 0.5–4 |
| \( \text{pH}_6 \) [-] | 1.9–2.1 | 1.9–2.1 | approx. 7 | 1.9–2.1 |
| Extraction temperature [°C] | 20 | | | |
| Extraction time [h] | 2 | | | |
| Rotation speed [rpm] | 60 | | | |

2.3. Determination of the Relationship between the Number of Theoretical Stages and the Phase Ratio with Numerical Methods

The classical technique for the determination of the number of theoretical stages is the graphical or numerical [35] solution of the McCabe–Thiele diagram. However, the calculation can be performed more efficiently with modern techniques that generate more output information. In this study, an algorithm has been developed to calculate the relationship between the number of theoretical stages and the phase ratio at equilibrium. The algorithm has been written in MATLAB R2019b and is available in the Supplementary Materials. It uses the “fsolve” function and solves the system of equations derived from the molar balance for the counter-current multistage extraction illustrated in Figure 2.
The molar balance in the first extraction stage for an extracted component in a volume element $V_{AP}$ (Equation (4)) and $V_{OP}$ (Equation (5)) consists of three terms: molar flow into the system ($\dot{n}_{AP,IN}$, $\dot{n}_{OP,N-1}$), molar flow out of the system ($\dot{n}_{AP,1}$, $\dot{n}_{OP,OUT}$) and mass transfer ($\dot{n}_{MS,1}$).

$$\dot{n}_{AP} = \dot{n}_{AP,IN} - \dot{n}_{AP,1} - \dot{n}_{MS,1}$$  \hspace{1cm} (4)  
$$\dot{n}_{OP} = \dot{n}_{OP,N-1} - \dot{n}_{OP,OUT} + \dot{n}_{MS,1}$$  \hspace{1cm} (5)  

Considering the correlation $n = c \cdot V$ the molar balance for both phases can be expressed as a function of concentration (Equations (6) and (7)).

$$\dot{c}_{AP} = \frac{\dot{V}_{AP}(c_{AP,IN} - c_{AP,1}) - \dot{n}_{MS,1}}{V_{AP}}$$  \hspace{1cm} (6)  
$$\dot{c}_{OP} = \frac{\dot{V}_{OP}(c_{OP,N-1} - c_{OP,OUT}) + \dot{n}_{MS,1}}{V_{OP}}$$  \hspace{1cm} (7)  

According to the two-film theory the mass transfer ($\dot{n}_{MS,1}$) is given by Equation (8).

$$\dot{n}_{MS,1} = K_{L,a}(c_{AP,1} - c_{AP,eq}) \cdot V_{AP}$$  \hspace{1cm} (8)  

where $K_{L,a}$ is the volumetric mass transfer coefficient and $c_{AP,eq}$ the equilibrium concentration of the extracted component in the aqueous phase. The equilibrium concentration $c_{AP,eq}$ is a function of $c_{OP,eq}$ and can be determined experimentally by performing curve fitting to the data points generated by changing the phase ratio and/or the initial boric acid concentration in the aqueous phase. The computation with MATLAB was performed for the steady state case, and the following assumptions were made:

- The volume of organic and aqueous phase is much greater than volume flow (residence time $V_{OP}/\dot{V} = V_{AP}/\dot{V} = 1000$ h);
- The mass transfer is very fast ($K_{L,a} = 1000$/h);
- The volume of the organic and aqueous phase remains constant during the extraction process.

3. Results and Discussion

3.1. Effect of ROH Concentration on Distribution Ratio and on Viscosity of Organic Phase

First, the effect of the concentration of the monohydric alcohols diluted in kerosene on the distribution ratio (D) of boric acid was investigated. The results are illustrated in Figure 3. Monohydric alcohols with a steric hindrance at $\alpha$-carbon atom (2-octanol; 3,7-dimethyl-3-octanol, see Figure 1) have a low extraction efficiency for boric acid. The max-
imal determined distribution coefficients ($D_{2\text{-octanol,MAX}}$, $D_{3,7\text{-dimethyl-3-octanol,MAX}}$) were 0.095 and 0.037, respectively. In the case of an unbranched alcohol ($n$-octanol), the distribution coefficient was roughly proportional to the concentration of the extractant and the maximal determined value was 0.180. The result is comparable to the distribution coefficient determined by J. Hejda and V. Jedinkova (1983) [36] which is $D_{n\text{-octanol}} = 0.168$. In comparison, the $c_{\text{ROH}}$-D-relationship for alcohols with a steric hindrance at $\beta$-carbon atom ($2\text{-ethyl-1-hexanol; 2-butyl-1-octanol}$) was not linear. The distribution coefficient increased sharply up to an extractant concentration of 4 mol/L for 2-ethyl-1-hexanol, and of 3 mol/L for 2-butyl-1-octanol. Higher concentrations of both alcohols did not lead to a significant increase of the extraction of boric acid. The maximal distribution ratio was approximately twice as high as that of $n$-octanol ($D_{2\text{-ethyl-1-hexanol,MAX}} = 0.353$; $D_{2\text{-butyl-1-octanol,MAX}} = 0.356$). The main conclusion of this comparison is that the extraction efficiency depends on the structure of the carbon chain of monohydric alcohols. More precisely, the distance between the steric hindering alkyl chain and the hydroxyl group is crucial for a high extraction efficiency of monohydric alcohols for boric acid. The similar maximal values for $D_{2\text{-ethyl-1-hexanol,MAX}}$ and $D_{2\text{-butyl-1-octanol,MAX}}$ indicate that the length of the steric hindrance obviously does not play a major role.

Figure 3. Effect of concentration (a) and volume fraction (b) of the monohydric alcohol diluted in kerosene on the distribution coefficient (experiment (I), Table 1).
Aside from the extraction efficiency, the physical properties such as the viscosity of the organic phase ($\mu$) and water solubility of the extractant are crucial for a successful industrial application. The effect of ROH concentration on the viscosity of mixtures of $n$-octanol, 2-ethyl-1-hexanol and 2-butyl-1-octanol in kerosene is illustrated in Figure 4.

In all three cases, the viscosity of the organic phase was similar up to a volume fraction of the extractant of about 50%. At the volume fraction of 50%, the viscosity was about twice as high as that of kerosene. At higher concentrations, the viscosity increased sharply, especially in the case of 2-butyl-1-octanol. Therefore, 2-butyl-1-octanol required a higher dilution compared to 2-ethyl-1-hexanol and $n$-octanol. However, 2-butyl-1-octanol showed the lowest solubility in water compared to all other monohydric alcohols considered in this study, which was $<1$ mg/L (Table 2).

![Figure 4. Effect of alcohol (ROH) concentration on the viscosity of n-octanol, 2-ethyl-1-hexanol and 2-butyl-1-octanol diluted in kerosene.](image)

Table 2. Solubility of $n$-octanol (1), 2-ethyl-1-hexanol (2), 2-butyl-1-octanol (3), 2-octanol (4), and 3,7-dimethyl-3-octanol (5) in water at 20 °C [37].

| Compound | (1) | (2) | (3) | (4) | (5) |
|----------|-----|-----|-----|-----|-----|
| solubility in water [g/L] | 0.30 | 0.60 | <0.001 | 1.12 | 0.32 |

3.2. Slope Analysis

The stoichiometry of the extraction species (x and y, Equation (9)) could be determined by performing the slope analysis.

$$[xH_3BO_3]_{AP} + [yROH]_{OP} \leftrightarrow [ROH_y(H_3BO_3)_x]_{OP}$$  \hspace{1cm} (9)

The linearization of the mass action law equation of an extraction reaction provides the molar proportion of extractant and extracted species. The successful application of the method assumes that, with the exception of extraction process (Equation (9)), no other interactions in the organic and aqueous phase take place. However, according to the literature, alcohols are considered to associate into a series of n-mers [38]. The determination of the stoichiometry for the extraction of boric acid with alcohols by the slope analysis fails as a consequence of this self-association (Figure 5).

The determined slopes for $n$-octanol, 2-ethyl-1-hexanol and 2-butyl-1-octanol were 0.64, 0.58 and 0.68, respectively; this indicated an approximate ratio of 2:1 (H$_3$BO$_3$:ROH). Zhang et al. (2016) [21] and Peng et al. (2018) [22] obtained similar results. The authors
explained this deviation by the slow kinetics of esterification as well as by other molecular interactions. However, the authors did not specify these interactions.

According to Hejda and Jedinakova (1983) [36], considering the effective concentration of alcohol, the stoichiometric coefficients x and y by the extraction of boric acid with n-hexanol are 1 and 3, respectively. Moreover, it has also been found that a formation of the ester \( B(OC_6H_{13})_3 \) probably takes place. Therefore, the general statement of Brown and Sanderson (1980) [3] that the extraction of boric acid by monohydric alcohols is caused by purely physical actions is not valid. Most probably, physical actions as well as chemical reactions between molecules of boric acid and monohydric alcohols take place to different extents. To clarify this statement, more detailed studies are needed.

\[
I = \frac{1}{2} \sum_{i=1}^{n} c_i \cdot z_i^2
\]

\( c_i \)—molar concentration of ion i [mol/L]

\( z_i \)—charge number of ion i

Figure 5. Determination of the stoichiometry of the extraction species by slope analysis.

3.3. Effect of Ionic Strength on Distribution Ratio

In this section, the effect of ionic strength on the distribution ratio using different salts (NaCl, MgCl\(_2\), Na\(_2\)SO\(_4\), LiNO\(_3\), LiCl) is investigated. In the beginning, 2-ethyl-1-hexanol dissolved in kerosene with a concentration 4.46 mol/L (70 vol\%) was used as an organic phase. The ionic strength (I) is calculated by Equation (10), and the results are illustrated in Figure 6a).

\[
\text{With the exception of Na}_2\text{SO}_4, \text{ the distribution ratio increased with the increase in ionic strength. Regarding Na}_2\text{SO}_4 \text{ the deviation may have been caused by interactions of boric acid with sulfate ions or by their co-extraction by 2-ethyl-1-hexanol. The co-extraction of sulfate ions is examined in Section 3.4 in more detail.}

\text{Compared to MgCl}_2, \text{ LiCl and LiNO}_3, \text{ the presence of NaCl salt in the aqueous phase had the smallest effect on the distribution ratio. By contrast, the presence of lithium chloride salts caused the strongest increase in the ability to extract boric acid. According to Brown and Sanderson (1980) [3] the presence of magnesium chloride has the strongest impact on the distribution ratio compared to other chlorides such as LiCl, NaCl, CaCl}_2. \text{ However, this statement refers to the salt concentration and not to the value of ionic strength (Figure 6a,b). Due to the higher charge number of magnesium ions in comparison to lithium ions and due to the resulting higher concentration of negatively charged ions, the value of ionic strength was three times higher in the case of MgCl}_2 \text{ than the salt concentration. The main}
\]
conclusion of the investigation is that, among the investigated salts, lithium chloride has the strongest impact on the distribution ratio of boric acid when considering the ionic strength and not the ion concentration.

Another important point is the extent of the increase in the distribution ratio. It was possible to achieve a distribution ratio higher than 6 by increasing the ionic strength to 12 mol/L. In comparison to the aqueous phase without any salt, the distribution ratio was approximately 17 times greater (Figure 3). Consequently, it can be stated that 2-ethyl-1-hexanol is a powerful extractant for boric acid only in combination with a high ionic strength. According to Zhang et al. (2016) [21] the distribution ratio can be even higher than 10 when conducting the extraction experiments with a magnesium-rich brine. It is also important to note that, in comparison to 1,3-diols, which show distribution ratios in the range of 10.7–31.7 [39], the extraction efficiency of 2-ethyl-1-hexanol in combination with a high ionic strength is of the same order. Therefore, the consideration that monohydric alcohols are rather ineffective extractants for boric acid is not entirely accurate.

In comparison to n-octanol and 2-butyl-1-octanol, 2-ethyl-1-hexanol showed the highest distribution ratio at high ionic strength (Figure 7). Furthermore, the difference in the distribution ratio increased with the increase in the ionic strength.
3.4. Co-Extraction of Salting-Out Agent

In this section, the co-extraction of different salting-out agents (Na$_2$SO$_4$, NaCl, MgCl$_2$, LiNO$_3$ and LiCl) is investigated. For this purpose, the loaded organic phases (70 vol% of 2-ethyl-1-hexanol diluted in kerosene) obtained in extraction experiment (2) were stripped with water at a phase ratio of 1, and the concentration of sulfur, sodium, magnesium and lithium in stripping water was determined.

The concentration of sulfur in the stripping water was below the detection limit of 0.1 mg/L. This indicates that the co-extracted amount of Na$_2$SO$_4$ by 2-ethyl-1-hexanol was negligible. Consequently, the decrease in the distribution ratio with the increase in the concentration of Na$_2$SO$_4$ was most probably caused by interactions of boric acid with sulfate, hydrogen sulfate ions and/or sulfuric acid molecules present in the aqueous phase. The suggested structure of the association complex is depicted in Figure 8.

In addition, the sodium content in solutions belonging to extraction experiments with NaCl was low in all three cases and did not exceed a value of 70 µmol/L (Figure 9). Consequently, the co-extraction of NaCl can be neglected as well.

As opposed to this, relevant quantities of lithium as well as magnesium in stripping solutions were detected, especially at high concentration of salting-out agent in the initial solutions. This implies that MgCl$_2$, LiNO$_3$ and LiCl are co-extracted by 2-ethyl-1-hexanol,
and the extent of the co-extraction increases with the concentration of salting-out agent. It is also important to note that the amount of co-extracted LiNO$_3$ was twice as much as the of LiCl. In summary, it can be stated that salting-out agents that affect the extraction efficiency positivity are co-extracted. The contamination of the stripping solution can have a negative effect on the purity of the obtained boric acid.

![Figure 9](image)

**Figure 9.** Effect of salting out agent and its concentration in the aqueous phase on the co-extraction of Na$^+$, Mg$^{2+}$, Li$^+$.  

3.5. Determination of the Relationship between the Number of Theoretical Stages and the Phase Ratio with MATLAB

In this section, the calculation of the number of required theoretical stages at different phase ratios with the model presented in Section 2.3 is presented. The calculation was performed for the solvent extraction of boric acid with 2-ethyl-1-hexanol dissolved in kerosene (70 vol%) from two different aqueous phases, without any salt (case 1) and with the addition of 4 mol/L of MgCl$_2$ (case 2). The initial concentration of boric acid in both solutions was 2 g/L (185 mmol/L; concentration of boric acid in Salar de Atacama Brine: 2.3–3.9 g/L [33]) and was reduced to <5 mg/L (<4 mmol/L; extraction yield >98%; average boron concentration in sea water [40]).

The experimental results and the corresponding fitting functions for equilibrium concentration $c_{H_3BO_3,AP,eq}$ for both cases are illustrated in Figure 10. The relationship between the phase ratio and the stage number calculated with MATLAB model as well as the corresponding extraction yields are depicted in Figure 11.

![Figure 10](image)

**Figure 10.** Experimentally determined relationship between the equilibrium concentration of boric acid in the aqueous and the organic phase for case 1 and 2 (experiment (4), Table 1).
3.5.1. Case 1

In the case of the extraction from aqueous phase without any salt, the dependence between equilibrium concentration in the aqueous and the organic phase was nearly linear (Figure 10). A straight line was fitted to the data points. As depicted in Figure 11, due to the low distribution ratio of the considered system, the removal of boric acid could be achieved only at a high stage number (high investment costs) or at high phase ratios (high operating costs). For example, at a phase ratio of three, 22 extraction stages were needed for the reduction of boric acid concentration from 185 mmol/L to \(< 4\) mmol/L. As illustrated in Figure 11, between the two value pairs (PR; SN) of (3.5; 10) and (4.5; 6), the investment as well as operating costs are the lowest. However, the removal of boric acid in an extraction process with six to 10 extraction stages and at a phase ratio between 3.5 and 4.5 does not appear to be the method of choice.

To verify the accuracy of the MATLAB algorithm, a McCabe–Thiele diagram for a phase ratio of 4 was solved graphically (Figure 12). The graphical method provided the same number of theoretical stages (seven) as the MATLAB model. Its correctness is therefore confirmed.
3.5.2. Case 2

For the solvent extraction of boric acid from an aqueous phase containing 4 mol/L MgCl₂, a polynomial of the second grade was fitted to the experimental data points (Figure 10). Compared to the process without the addition of salting-out agent, the value pairs of the stage number and the phase ratio were much lower (Figure 11). The minimums of the operating as well as investment costs were between the following value pairs: (0.5; 3.0) and (1; 2). Consequently, the optimal phase ratio and the stage number were between 0.5–1.0 and 2–3, respectively.

4. Conclusions

This study presents a detailed overview of the solvent extraction of boric acid with monohydric alcohols. From all results generated in this work, a general correlation between the structure of the carbon chain, the composition of the aqueous phase and the extraction performance of monohydric alcohols can be derived, which is outlined in Table 3.

Table 3. Correlation between the structure of the carbon chain and the relative extraction performance of monohydric alcohols calculated with D_{ROH}/D_{n-octanol} (3,7-dimethyl-3-octanol (1), 2-octanol (2), n-octanol (3), 2-ethyl-1-hexanol (4), and 2-butyl-1-octanol (5)).

| Alcohol | Special feature of carbon chain | Relative extraction performance without salting out agent | Relative extraction performance at an ionic strength of 16 mol/L |
|---------|---------------------------------|--------------------------------------------------------|-------------------------------------------------------------|
|         | Tertiary a-carbon                | 0.20                                                   | Not determined                                              |
|         | Secondary a-carbon               | 0.53                                                   | Not determined                                              |
|         | Unbranched carbon chain          | 1.00                                                   | 10.28                                                      |
|         | Secondary β-carbon               | 1.96                                                   | 34.33                                                      |
|         |                                  | 1.98                                                   | 17.78                                                      |

The main conclusion of the work is that the ability to extract boric acid depends strongly on the position of a steric hindrance. From all tested compounds, the monohydric alcohols with a steric hindrance at β-carbon atom showed the highest extraction efficiency. Another very important factor for the effective solvent extraction of boric acid with monohydric alcohols is the presence of a salting-out agent; without any salt in the aqueous phase, the distribution ratio does not exceed a value of 0.4. The calculated relationship between the stage number and the phase ratio with MATLAB makes it evident that the removal of boric acid from such systems is not economically feasible. Monohydric alcohols are powerful extractants only in connection with a high salt concentration in the aqueous phase. The order of the distribution ratio of 2-ethyl-1-hexanol at a high ionic strength is comparable to those of diols. Nevertheless, the co-extraction of a salting-out agent leads to the contamination of boric acid obtained by water stripping. Of all tested monohydric alcohols, 2-ethyl-1-hexanol shows the highest extraction efficiency. However, its solubility in the aqueous phase is much higher than that of 2-butyl-1-octanol. Nevertheless, referring to 2-ethyl-1-hexanol, the viscosity of the organic phase at high ROH concentration is lower.

Supplementary Materials: The following are available online at https://www.mdpi.com/2227-9717/9/2/398/s1, model.zip.

Author Contributions: Conceptualization, A.B.; methodology, A.B.; validation, N.K., V.R.; investigation, A.B.; resources, A.B.; writing—original draft preparation, A.B.; writing—review and editing, N.K., V.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the BMBF (Federal Ministry of Education and Research, Germany); funding number: 033R132A.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.
Acknowledgments: The authors sincerely thank Stefanie Schubert for the chemical analysis of liquid phases and Christina Meskers, Markus Reuter and Jens Gurzmer for their discussion and comments on earlier versions of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

Abbreviations
The following abbreviations are used in this manuscript:

- AAS: Atomic absorption spectroscopy
- AP: Aqueous phase
- c: Molar concentration
- D: Distribution ratio
- eq: Equilibrium
- I: Ionic strength
- ICP-OES: Inductively coupled plasma optical emission spectrometry
- $K_{l,a}$: Volumetric mass transfer coefficient
- MS: Mass transfer
- $\mu$: Viscosity
- n: mol
- OP: Organic phase
- PR: Phase ratio
- ROH: Alcohol
- SN: Stage number
- V: Volume
- z: Charge number

References
1. Mergen, A.; Demirhan, M.H.; Bilen, M. Processing of boric acid from borax by a wet chemical method. Adv. Powder Technol. 2003, 14, 279–293. [CrossRef]
2. Kistler, R.B.; Helvaci, C. Industrial Minerals and Rocks; Donald, D.C., Ed.; Society for Mining and Metallurgy and Exploration Inc.: Littleton, CO, USA, 1994; pp. 171–186.
3. Brown, C.G.; Sanderson, B.R. Solvent extraction of boron. Chem. Ind. 1980, 68–73.
4. Cramer, T.M. Production of Boric Acid and Sodium Nitrate. U.S. Patent US2965446A, 20 December 1960.
5. ZareNezhad, B. Experimental and theoretical investigation of boron production through reactive dissolution of oxalic acid crystals in borax aqueous solution. Korain J. Chem. Eng. 2003, 20, 44–47. [CrossRef]
6. ZareNezhad, B. Direct production of crystalline boric acid through heterogeneous reaction of solid borax with propionic acid: Operation and simulation. Korain J. Chem. Eng. 2004, 21, 956–962. [CrossRef]
7. Kusaky, B.; Bulutcu, A.N. Design parameters of boric acid production process from colemanite ore in the presence of propionic acid. Chem. Eng. Process. Process. Intensif. 2011, 50, 377–383. [CrossRef]
8. Bulutcu, A.N.; Ertekin, C.O.; Kuskay Celikoyan, M.B. Impurity control in the production of boric acid from colemanite in the presence of propionic acid. Chem. Eng. Process. Process. Intensif. 2008, 47, 2270–2274. [CrossRef]
9. Polendo-Loredo, J. Process for the Preparation of Boric Acid from Colemanite and/or Howlite Minerals. U.S. Patent US4804524A, 14 February 1989.
10. Elbeyli, I.Y.; Turan, A.Z.; Kalafatoglu, I.E. The electrochemical production of boric acid. Chem. Ind. 2015, 90, 1855–1860.
11. Erkmen, J.; Yapici, S. A environmentally friendly process for boric acid and sodium hydroxide production from borax; bipolar membrane electrochemical. Desalin. Water Treat. 2016, 57, 20261–20269. [CrossRef]
12. Zahid Turan, A.; Elbeyli, I.A.; Bahar, T.; Kalafatoglu, I.E. The performance of Nafion®424 in the membrane electrolysis of borax solution. J. Ind. Eng. Chem. 2012, 18, 1102–1106. [CrossRef]
13. An, J.W.; Kang, D.J.; Tran, K.T.; Kim, M.J.; Lim, T.; Tran, T. Recovery of lithium from Uyuni salar brine. Hydrometallurgy 2012, 117–118, 64–70. [CrossRef]
14. Flexer, V.; Baspineiro, C.I. Lithium recovery from brines: A vital raw material for green energies with a potential environmental impact in its mining and processing. Sci. Total Environ. 2018, 639, 1188–1204. [CrossRef] [PubMed]
15. Boryta, D.A.; Kullberg, T.F.; Thurston, A.M. Production of Lithium Compounds Directly from Lithium Containing Brines. U.S. Patent US7449161B2, 11 November 2008.
16. Wilkomirsky, I. Process for Extracting the Boron Content in the Brine of Natural or Industrial Salt Mine. U.S. Patent US4804524A, 14 October 1997.
17. Wilkomirsky, I. Extraction of Boron from Brines Having a pH of Less than about 1.7 Using Beta-Aliphatic Diols. U.S. Patent US3493349A, 3 February 1970.

18. Grinstead, R.R. Removal of boron and calcium from magnesium chloride brines by solvent extraction. Ind. Eng. Chem. Prod. Res. Dev. 1972, 11, 454–460. [CrossRef]

19. Fan, X.; Yu, X.; Guo, Y.; Deng, T. Recovery of boron from underground brine by continuous centrifugal extraction with 2-Ethyl-1,3-hexanediol (EHD) and its mechanism. J. Chem. 2018, 2018, 7530837. [CrossRef]

20. Guo, J.; Yang, Y.; Gao, X.; Yu, J. Boron extraction from lithium-rich brine using mixed alcohols. Hydrometallurgy 2020, 197, 105477. [CrossRef]

21. Zhang, R.; Xie, Y.; Song, J.; Xing, L.; Kong, D.; Li, X.-M.; He, T. Extraction of boron from salt lake brine using 2-ethylhexanol. Hydrometallurgy 2016, 160, 129–136. [CrossRef]

22. Peng, X.; Li, L.; Shi, D.; Zhang, L.; Li, H.; Nie, F.; Song, F. Recovery of boric acid from salt lake brines by solvent extraction with 2-butyl-1-n-octanol. Hydrometallurgy 2018, 177, 161–167. [CrossRef]

23. Schilde, U.; Uhlemann, E. Extraction of boric acid from brines by ion exchange. Int. J. Miner. Process. 1991, 32, 295–309. [CrossRef]

24. Schilde, U.; Uhlemann, E. A simple method for the control of ion-exchange processes with boric acid using specific chelating resins. React. Polym. 1992, 18, 155–158. [CrossRef]

25. Blasdale, W.C.; Slansky, C.M. The solubility curves of boric acid and the borates of sodium. J. Am. Chem. Soc. 1939, 61, 917–920. [CrossRef]

26. Tsuboi, I.; Kunugita, E.; Komasawa, I. Recovery and purification of boron from coal fly ash. J. Chem. Eng. Jpn. 1990, 23, 480–485. [CrossRef]

27. Garrett, D.E. (Ed.) Part 1—Lithium. In Handbook of Lithium and Natural Calcium Chloride; Academic Press: Oxford, UK, 2004; pp. 1–235.

28. John, M.K.; Chuah, H.H.; Neufeld, J.H. Application of improved azomethine-H method to the determination of boron in soils and plant. Anal. Lett. 1975, 8, 559–568. [CrossRef]

29. Warade, A.; Gaikwad, R.; Sapkal, R.; Sapkal, V. Simulation of multistage countercurrent liquid-liquid extraction. Leonardo J. Sci. 2011, 20, 79–94.

30. Hejda, J.; Jedinaňková, V. Separation of boric acid from radioactive wastes by liquid-liquid extraction. J. Radioanal. Chem. 1983, 80, 23–29. [CrossRef]

31. Fletcher, A.N.; Heller, C.A. Self-association of alcohols in nonpolar solvents. J. Phys. Chem. 1967, 71, 3742–3756. [CrossRef]