Recovery of boron from unacidified salt lake brine by solvent extraction with 2,2,4-trimethyl-1,3-pentanediol

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Abstract

The recovery of boron from salt lake brine using 2,2,4-trimethyl-1,3-pentanediol was investigated. Factors affecting boron recovery, including pH, concentrations of extractant and H3BO3, phase ratio(O/A), and temperature, were investigated. Increasing pH initially resulted in high extraction rate, but there was a limitation, as further increasing pH resulted in rapid formation of B[OH]4- having a low capacity to complex with TMPD, and therefore lower boron extraction. Boron recovery increased as the TMPD and O/A increased. The combination of pH <7, O/A=1 & n(TMPD/H3BO3)=2:1 was ideal for boron recovery, resulting in extraction efficiency of >85%. To investigate extraction mechanism, slope ratio method was combined with Raman and infrared spectroscopy to characterize the structure of complex. Furthermore, under optimal conditions, a three-stage extraction and two-stage stripping process was performed, resulting extraction and stripping efficiency were 97.12% and 88.98%, respectively. The results reveal a promising strategy of boron recovery from SL brine without acidification.

Recovery of boron from unacidified salt lake brine bysolvent extraction with 2,2,4-trimethyl-1,3-pentanediol

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Abstract: In this work, the extraction of boron from salt lake (SL) brine using 2,2,4-trimethyl-1,3-pentanediol (TMPD) was investigated. Factors affecting boron recovery during the solvent extraction process, including feed pH, concentrations of extractant and H_3BO_3, phase ratio of organic to brine (O/A), and temperature, were investigated. Increasing feed pH initially resulted in a high boron extraction rate, but there was a limitation, as further increasing feed pH resulted in rapid formation of $B[OH]_4^-$ having a low capacity to complex with TMPD, and therefore lower boron extraction. Boron recovery increased as the TMPD concentration and O/A increased. Salting-out effect experiment indicated that the addition of magnesium chloride showed two opposite effects on boron extraction. The combination of pH <7, O/A=1 & TMPD/H_3BO_3 molar ratio=2:1 was ideal for boron recovery, resulting in boron extraction efficiency of >85%. To investigate the extraction mechanism, the slope ratio method was combined with Raman spectroscopy and infrared spectroscopy to characterize the structure of TMPD and boron complex in organic extraction solvent. Furthermore, under the optimal conditions, a three-stage extraction and two-stage stripping process was performed, resulting

the extraction and stripping efficiency of boron were 97.12% and 88.98%, respectively. The results of the study reveal a promising strategy of boron recovery from SL brine without acidification.

Key Words: Boron recovery; TMPD; Extraction complex; Salt lake brine

1. Introduction

The special properties of boron and its compounds make it an important application in various industries as a raw material[1,2]. The raw materials of boron are mainly derived from solid boron ore and brine ore. During exploitation of salt lake brine, high-efficiency separation of boron can lead to high-quality boric acid products, while minimizing influence of boron on the quality of valuable elements such as lithium and magnesium[3]. For the recovery of boric acid, several methods which have been studied are boron precipitation[4,5], adsorption[6-8], membrane filtration[9,10], electrodialysis[11,12], reverse osmosis[13,14], solvent extraction[15-17]. However, most of these processes are unsuitable for SL industrial application due to the low boron recovery rate and the high concentration of brine components. On the other hand, low capital cost and relatively simple operation technique make solvent extraction a promising process of large-scale application for recovering boric acid from SL brine. Thus, solvent extraction process has been widely employed to recover boron from SL brine.

In general, unitary alcohols, diols and some polyols have excellent properties for boron extraction[18,19]. Among these extractants, diols have demonstrated a high extraction efficiency over a wider pH range since diols can form relatively stable five-membered or six-membered cyclic borate compounds with boron[20], especially 1,3-diols are considered to be the most effective. Narbutt et al.[21] used 2-ethyl-1,3-hexanediol and 2-ethyl-2-butyl-1,3-propanediol to extract boron from radioactive corrosion and fission products dissolved in aqueous solutions. Karakaplan et al.[22] synthesized 9 different 1,3-diols and compared the boron extraction effects of the synthesized extractants, in which 2,2,4-trimethyl-1,3-pentanediol and 2,2,5-trimethyl-1,3-hexanediol had a high extraction effect. The results showed that the extractant had good extraction performance for boric acid, with a single-stage extraction rate of >95%. Hano et al.[23] studied that 2-ethyl-1,3-hexanediol (EHD) dissolved in kerosene is considered to be the best extractant to remove and recover boron from hot spring water. When the pH value was 1~8, the extraction rate reached 90%, but it decreased when the pH was greater than 8. However, due to the high solubility of EHD in water, EHD is not considered suitable for practical application in boron removal from water. The extraction of boron using 2-butyl-2-ethyl-1,3-propanediol and 2-ethylhexanol at different boron and extractant concentrations was investigated by Kwon et al.[24]. The results of equilibrium concentration of the extractants on distribution of boron indicates that the mechanism of boron extraction by these extraction systems is the same.

The SL in the Qaidam Basin of China is rich in boron resources. However, at present, the extraction process of boron from SL brine in Qaidam, Qinghai province, China is to acidify the brine first, and then extract boric acid by monoalcohol extraction system[25]. The acidification process will precipitate a large amount of boric acid, resulting in an increase in production costs and a low recovery rate of boric acid. Therefore, a new process needs to be found to remove the brine acidification process.

In this contribution, a 1,3-diol, 2,2,4-trimethyl-1,3-pentanediol (TMPD) was introduced to examine the possibility of extracting boron from SL brine without acidification. The optimal extraction parameters were determined by performing extraction experiments under the influence of different factors. The entire extraction process was carried out by the separation funnels, and the organic materials were recycled and reused. Furthermore, we investigated the mechanism of the complexes formation by means of Raman spectroscopy, IR spectroscopy and the slope ratio method.

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2. Materials and methods

2.1 Materials

The extractant TMPD (97%) and the diluent CCl_4 (97%) were purchased from TCI Co. Ltd.. Boric acid (99.5%), purchased from Tianjin Kemi'ou Chemical Reagent Co., was used as the boron source. Ultrapure water was used in all experiments. The simulated brine was prepared by dissolving H_3BO_3 in saturated magnesium chloride solution or ultrapure water, while the pH value of experimental solutions was adjusted using HCl or NaOH. All reagents were of analytical grade and were used without further purification.

The SL brine used in this study was collected from the Xitaijiner SL (located in the central part of the Qaidam Basin in China) and provided by Qinghai Citic Guoan Co.. The main characteristics of the brine are presented in Table 1.

Table 1. Main characteristics of the brine.

ρ (g/cm^3)	pH	Ions Conc. (mol/L)	Ions Conc. (mol/L)	Ions Conc. (mol/L)	Ions Conc. (mol/L)	Ions Conc. (mol/L)
		H_3BO_3	Li^+	Mg^{2+}	Na^+	K^+
1.30	4.60	0.20	0.28	4.27	0.21	0.026

2.2 Single-stage extraction procedures

The extraction experiments were conducted and duplicated in separatory funnels. At ambient temperature (293±1 K), a mixture containing a certain volume of the aqueous and organic phase was subjected to mechanical vibration at 300 r/min, and then let it stand until the two phases separated. Contact time was selected after preliminary extraction experiments, for a period of 10 min, which was found enough for equilibrium. Then, the aqueous and organic samples were collected for further analysis.

The organic solution used in all experiments was composed of 0.4 mol/L TMPD dissolved in CCl_4, and the phase ratio was 1/1 (O/A), except when explicitly described otherwise. In order to investigate the effects of pH, the concentration of H_3BO_3 and the concentration of $MgCl_2$ on boron extraction, three simulated brines (which are listed in Table 2) were prepared, respectively, while the filtered SL brine (given in Table 1) was used in the experiment of other factors, including the concentration of TMPD, the phase ratio (O/A) and the temperature. All single factor experiments were performed at room temperature, except when studying the effect of temperature, according to procedures described above.

Table 2. Main characteristics of the simulated brines.

Simulated brines	pH	H_3BO_3, mol/L	$MgCl_2$, mol/L
Sb-1	1~10	0.20	0
Sb-2	6.0	0.08~0.60	0
Sb-3	1.3, 3.0, 4.6, 6.0	0.20	0~4.5

2.3 Multi-stage countercurrent extraction procedures

The three-stage countercurrent extraction as shown in Figure 1 was performed using a separatory funnels at a laboratory scale[26]. 0.4 mol/L TMPD dissolved in CCl_4 and the SL brine without acidification (pH=4.60) was used as organic phase and feed brine, respectively. Firstly, the prepared fresh organic (20 mL) and feed brine (20 mL) were added to the second funnel. After the mixture reached a balance, the phase separation was set. Then, the aqueous phase (A2) was poured into the first funnel and the organic phase (O2) into the third funnel. Equal volumes of the fresh organic and brine were then added to the first and the third

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stage for the mixture and separation, respectively. Then, the organic phase (O1) and aqueous phase (A3) were simultaneously poured into the second funnel, and both the raffinate and the loaded organic samples were obtained. In this way, the whole countercurrent extraction process could be recycled by introducing the feed brine and organic intermittently. After a series of extraction and product removal cycles, the system stabilized. The whole five-stage extraction and stripping process experiment (section 3.10) was carried out in the same way.
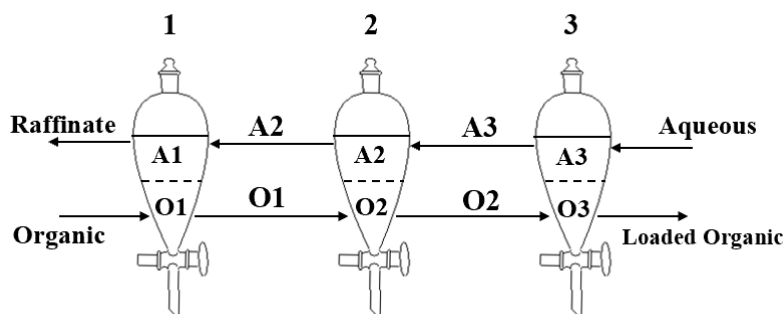

Fig. 1. Flow chart of three-stage continuous countercurrent extraction. The separatory funnel with numbers represents a single extraction. A(1-3) and O(1-3) represent the aqueous and organic phases after extraction to reach equilibrium, respectively.

2.4 Analysis

Metal ions concentration of aqueous phase was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (ICAP6500 DUO; America Thermo Scientific). The concentrations of boric acid in aqueous phase were determined by titration[27], but the trace amounts of boric acid were measured by ICP-AES. The boron in the organic phase was stripped into the aqueous for analysis, so the accuracy of the analysis can be verified by the mass balance of the boron in the two phases. The pH of all liquid samples was measured by a pH meter (Seven excellence, Mettler Toledo). After extraction, the organic phases with and without boron complexes were measured by FTIR spectra (Thermo Nicolet Corporation 670 Spectrometer). Raman spectrometer (DXR; American Thermo Fisher Scientific Co., Ltd.) has been used to characterize the presence of boron in the aqueous phase.

In this study, the extraction efficiency (E) and distribution ratio (D) were calculated by the formulas[28]:

$$E = \frac{V_{\text{org}} * [B]_{\text{org}}}{V_{\text{aq}} * [B]_{\text{aq}} + V_{\text{org}} * [B]_{\text{org}}} *100\% \quad \text{Eq. (1)}$$

$$D = \frac{[B]_{\text{org}}}{[B]_{\text{aq}}} \quad \text{Eq. (2)}$$

where $[B]_{org}$ and $[B]_{aq}$ are the equilibrium concentrations of boron in the organic and aqueous phases, respectively.

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3. Results and Discussion

3.1 Effects of the extraction parameters on H_3BO_3 Extraction

3.1.1 Effect of Feed pH

The pH of the aqueous solution has been considered as the crucial parameters affecting the H_3BO_3 extraction process[17,28]. To determine the effect of pH on H_3BO_3 extraction, experiments were performed at pH from 1 to 10 with a constant O/A of 1/1. As shown in Fig. 2, at a condition of initial aqueous pH value (abbreviated to pH_{ini}) less than 7, the extraction efficiency reached a stable level of 85%, and equilibrium aqueous pH value (abbreviated to pH_{eq}) reduced obviously comparing to the pH_{ini}. Meanwhile, the pH_{eq} and ΔpH (pH_{ini} -pH_{eq}) increased with the increasing of pH_{ini}. The extraction efficiency decreased sharply with the pH_{ini} continuously increasing, and the pH_{eq} was slight higher than pH_{ini}. It can be concluded that the extraction efficiency and pH_{eq} changed inversely, and a low extraction efficiency obtained when the pH_{eq} exceeded 9.4.

Boron is mainly present in natural water in the form of boric acid, and it appears as weak Lewis acid after hydrolysis.:

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Eq. (3)

Boric acid is mainly present in a condition with the pH value lower than 9.23, and in a higher pH environment, borate ion is the main form. It is well known that boric and borate ion can react with polyhydroxy compounds to form complexes[29]. The possible reaction mechanisms were shown in Fig. 3.

Fig. 2. Effect of simulated brine pH values on boron extraction. [TMPD] = 0.4 mol/L; O/A = 1.
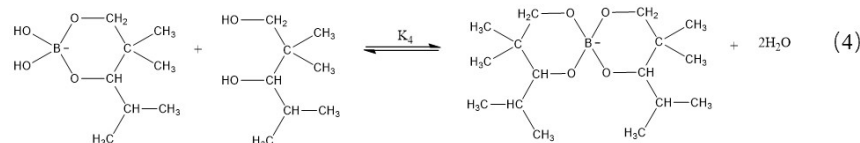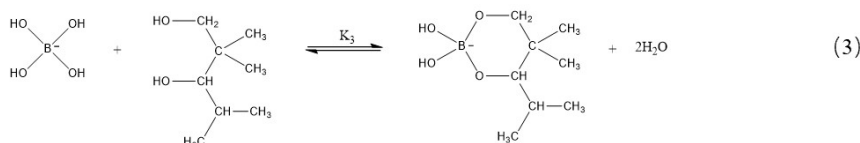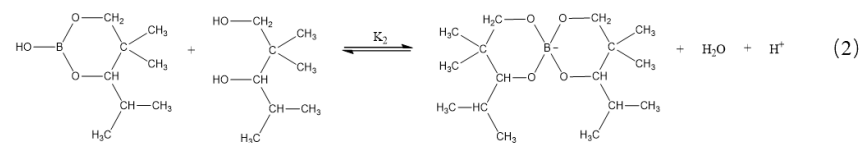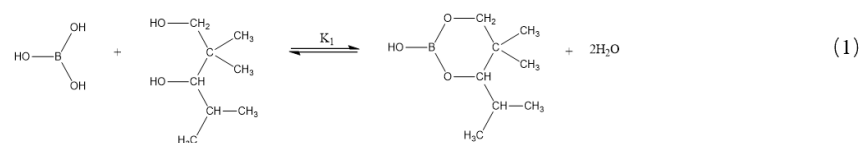

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Fig. 3. The possible reaction mechanisms

In acidic condition, TMPD complexed with H_3BO_3 by hydroxyl condensation and dehydration forming monocyclic boric acid ester, (Equilibrium equation 1), and the pH value had no change in this process. Excess TMPD reacted with monocyclic boric acid ester forming spiro boric acid ester, (Equilibrium equation 2), and H^+ released in this process. Formation of spiro boric acid ester and release H^+ made the pH value dicrease in the extraction process. The high extraction efficiency indicated that reaction 1 and 2 could easily perform. In alkaline condition, TMPD might complex with $[B(OH)_4]^-$ by hydroxyl condensation and dehydration forming boric acid esters, (Equilibrium equation 3 and 4), and the pH value had no change in these processes. The low extraction efficiency indicated that performation of reaction 3 and 4 was more difficult than the former.

3.1.2 Effect of TMPD concentration

The concentration of TMPD is an important factor affecting the equilibrium of boron extraction, and the stoichiometry of the complex of H_3BO_3 and TMPD can be calculated according to the effect of the TMPD concentration on the boron distribution ratio (D) by using the slope ratio method[30]. The experiments were carried out at the concentration of TMPD varied in range of 0.02~0.6 mol/L. It can be clearly seen from Fig. 4 that extraction efficiency and distribution ratio of H_3BO_3 both increase with the increasing of TMPD concentration.

As mentioned in section 3.1, boric acid can react with TMPD to form different boric acid esters and the formation of boric acid esters relate to the mole ratio of $TMPD/H_3BO_3$. The extraction equilibrium equation can be expressed as following formula:
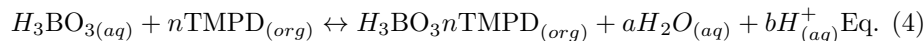
$H_3BO_{3(aq)} + nTMPD_{(org)} \leftrightarrow H_3BO_3nTMPD_{(org)} + aH_2O_{(aq)} + bH^+_{(aq)}$ Eq. (4)

Fig. 4. Effect of TMPD concentration on distribution ratio and extraction efficiency. pH_{ini} = 4.6; O/A = 1; $[H_3BO_3]_{ini}$ = 0.20 mol/L.

According to Eq. (4), the two-phase extraction equilibrium constant (K) could be given as follows:

$K = \frac{[H_3BO_3nTMPD]_{(org)}[H_2O]^a_{(aq)}[H^+]^b_{(aq)}}{[H_3BO_3]_{(aq)}[TMPD]^n_{(org)}}$ Eq. (5)

The $D_{H_3BO_3}$ value, which represents the distribution ratio of H_3BO_3 can be determined as follows:

$D_{H_3BO_3} = \frac{[H_3BO_3nTMPD]_{(org)}}{[H_3BO_3]_{(aq)}}$ Eq. (6)

Then, Eq. (5) can be transformed as follows:

$K = \frac{D_{H_3BO_3}[H_2O]^a_{(aq)}[H^+]^b_{(aq)}}{[TMPD]^n_{(org)}}$ Eq. (7)

By taking logarithms and rearranging, Eq. (7) convers to:

$\log D_{H_3BO_3} = logK + nlog[TMPD]_{(org)} - alog[H_2O]_{(aq)} - blog[H^+]_{(aq)}$ Eq. (8)

Keeping the initial pH of the aqueous phase unchanged, Eq. (8) can be represented as:

$\log D_{H_3BO_3} = nlog[TMPD]_{(org)} + C$ Eq. (9)

The value of n in Eq. (9) refers to the complex ratio between TMPD and H_3BO_3. The plots of $log D_{H_3BO_3}$ versus $log[TMPD]_{(org)}$ was shown in Fig. 5. When the mole ratio of TMPD and H_3BO_3 in initial two phases was less than 1:1, the slope was 1.17, which indicated that the complex ratio between TMPD and H_3BO_3 was 1. When the mole ratio of TMPD and H_3BO_3 in initial two phases was more than 1:1, the slope was 2.17, which indicated that the complex ratio between TMPD and H_3BO_3 was 2. This result indicated that the formation of the complex was connected with the concentration ratio of $TMPD/H_3BO_3$. It doesn't mean that below a certain ratio all esters are one form and above that they are all in another. Different complexes

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may co-exist when the extraction reaches equilibrium, and when TMPD is excessive, TMPD is more likely to form a 2:1 complex with boric acid.

Fig. 5. Plot of log D $_B$ vs log $[C$ $_{TMPD}]$. pH_{ini} = 4.6; O/A = 1; $[H_3BO_3]_{ini}$ = 0.20 mol/L.

3.1.3 Effect of H_3BO_3concentration

To understand the effect of H_3BO_3concentration on the extraction efficiency of H_3BO_3 in the simulated brine, batch experiments were performed at pH=6.0 with varying H_3BO_3 concentration (0.08~0.6 mol/L). The results are shown in Figures 6 and 7. The extraction efficiency of H_3BO_3decreased with the increasing of H_3BO_3concentration in aqueous phase, as can be seen from Fig. 6. The extracted H_3BO_3 in organic phase increased rapidly when the initial H_3BO_3 concentration below 0.4 mol/L. Continuous increasing initial H_3BO_3 concentration, the extracted H_3BO_3 did not increase, keeping a constant concentration of 0.25 mol/L.

Fig. 6. Variation in concentration of H_3BO_3 in organic phase and efficiency with the initial H_3BO_3concentration. [TMPD] = 0.4 mol/L; pH_{ini} =6.0; O/A = 1.

The mole ratio of TMPD and extracted H_3BO_3 decreased with the decreasing of the mole ratio of TMPD and H_3BO_3 in the initial two phases while the equilibrium pH of the raffinate changed inversely, as shown in Fig. 7. When the mole ratio of TMPD and H_3BO_3 in the initial two phases was greater than 2.12, the mole ratio of TMPD and extracted H_3BO_3 was greater than 2.38, which indicated that two TMPD molecular complexed with single H_3BO_3 molecular following Equilibrium 2, and amounts of TMPD molecular which had no effect on H_3BO_3 existed in organic phase. The released H^+ made the pH of aqueous decreased. With the mole ratio of TMPD and H_3BO_3 in the initial two phases decreasing from 2.12 to 0.87, the mole ratio of TMPD and extracted H_3BO_3 decreased from 2.38 to 1.59. Bimolecular complex and monomolecular complex occurred in this process following Equilibrium 1 and 2. The H^+ released in Equilibrium Equation 2 made the pH of aqueous decreased. The pH of aqueous showed a slight increase when the mole ratio of TMPD and H_3BO_3 in the initial two phases decreased from 5.10 to 0.87, which indicated that the proportion of Equilibrium 2 decreaced in this extraction process. Continuously decreasing the mole ratio of TMPD and H_3BO_3 in the initial two phases, the pH of raffinate had no significant difference from the initial simulated brine, and the mole ratio of TMPD and extracted H_3BO_3 kept a constant of 1.59. This indicated that Equilibrium 1 played the leading role, and the TMPD molecular complexed with H_3BO_3 molecular one by one. Similary to the higher mole ratio of TMPD and H_3BO_3 in initial two phases, amounts of TMPD molecular which had no effect on H_3BO_3 existed in organic phase.

Fig. 7. Variation in mole ratio of TMPD and extracted H_3BO_3 and equilibrium pH value of raffinate with respect to the mole ratio of TMPD and H_3BO_3 in initial two phases. pH_{ini} =6.0; O/A = 1; [TMPD] = 0.4 mol/L.

3.1.4 Effect of O/A

The influence of volume ratio of organic phase to aqueous phase (O/A) on boron extraction was investigated in the range of 0.2~2.5. It can be seen from Fig. 8 that the extraction efficiency of H_3BO_3 increased with the increasing of O/A while the concentration of H_3BO_3 in the organic changed inversely. The rate of improvement in extraction efficiency slowed down when O/A was greater than 1.0. When O/A was equal to 1, the single-stage extraction efficiency reached 86%, and the boron concentration of organic was 0.17 mol/L. Therefore, O/A of 1.0 is a more appropriate phase ratio condition. We then experimentally determined the maximum boron loading capacity of organic phase at 0.4 mol/L TMPD concentration was 0.40 mol/L (in H_3BO_3). When the phase ratio is 2.5, the extraction efficiency can reach 97%, but the boron content loaded in organic is only 0.078 mol/L, which is far less than the maximum boron loading capacity. Therefore, in order to improve the utilization rate of extractant and reduce the amount of extractant, multi-stage extraction must be adopted.

Fig. 8. Effect of O/A on the extraction efficiency of H_3BO_3. [TMPD] = 0.4 mol/L; pH_{ini} = 4.6.

3.1.5 Effect of Salting-out effect

Since SL brines in the Qaidam Basin usually contains high concentration of magnesium chloride[31,32], the salting-out effect of magnesium chloride on boron extraction process was investigated. Four groups of magnesium chloride solutions (0~4.5 mol/L) containing 0.20 mol/L H_3BO_3 were prepared as the aqueous phase, and the pH of the four groups was adjusted to 1.3, 3.0, 4.6, and 6.0, respectively. As shown in Fig. 9, with the continuous increase of $MgCl_2$, the difference of salting-out effect is obvious under different initial pH conditions: when the pH_{ini} is 1.3, the extraction efficiency of H_3BO_3 increases with the increase of the concentration of $MgCl_2$, which is a positive salting-out effect; when the pH_{ini} [?]3.0, the changes of the extraction efficiency of H_3BO_3 show a similar trend, first increasing, then decreasing and then increasing. Since the addition of $MgCl_2$ will promote the extraction of boric acid, and at the same time, it promotes the conversion of H_3BO_3 to $[B(OH)_4]^-$ and polyboronic oxide anions, resulting in the reduction of the extraction efficiency of H_3BO_3. Therefore, the obtained data is the experimental result that the two interactions reach a balance. It can be concluded that the addition of $MgCl_2$ does not always show positive salting-out effect for the dibasic alcohol extraction system, which is significantly different from the unary alcohol extraction system[25], and the lower the pH_{ini}, the more promoting effect of $MgCl_2$ on boric acid extraction obviously. Additionally, the SL brine (pH=4.6) contains 4.27 mol/L Mg ions (shown in table 2) and in this concentration, the extraction efficiency of single-stage exceeds 80%, which also indicates that the extraction process has a high extraction efficiency without acidification.

Fig. 9. Changes of extraction efficiency with the $MgCl_2$ concentration at different pH_{ini}, [TMPD] = 0.4 mol/L; O/A=1.

3.1.6 Effect of Temperature

The effect of temperature on boron extraction by TMPD was performed in the temperature range of 293~333 K. Fig. 10 shows the linear relationship between log D against $1/T$. Based on the slope of the straight line in Fig. 10, the enthalpy change (ΔH) of the extraction process can be calculated using the Van't Hoff equation:

$$\log D = -\frac{\Delta H}{2.303R} \frac{1}{T} + C \qquad \text{Eq. (10)}$$

where R is the universal gas constant (8.314 J·mol^{-1}*K^{-1}). The enthalpy change ΔH can be evaluated to be 17.24 kJ·mol^{-1}, indicating the extraction reaction is endothermic. Therefore, appropriately increasing the temperature is beneficial for the extraction of boron. The Gibbs free energy $\Delta \Gamma$ were calculated by:

$$\Delta \Gamma = -2.303RT \log K \qquad \text{Eq. (11)}$$

Two equilibrium constant K values under different conditions were obtained from the fitting curve in the Fig. 5. Consequently, the changes in free energy at 293 K are calculated as follows: $\Delta \Gamma$ = -5.20 kJ·mol^{-1} when the mole ratio of TMPD and H_3BO_3 in initial two phases is less than 1:1, and $\Delta \Gamma$ = -9.42 kJ·mol^{-1} when the mole ratio of TMPD and H_3BO_3 in initial two phases is more than 1:1. Both are negative values, indicating that the extraction of boric acid by $TMPD/CCl_4$ extraction system can proceed spontaneously.
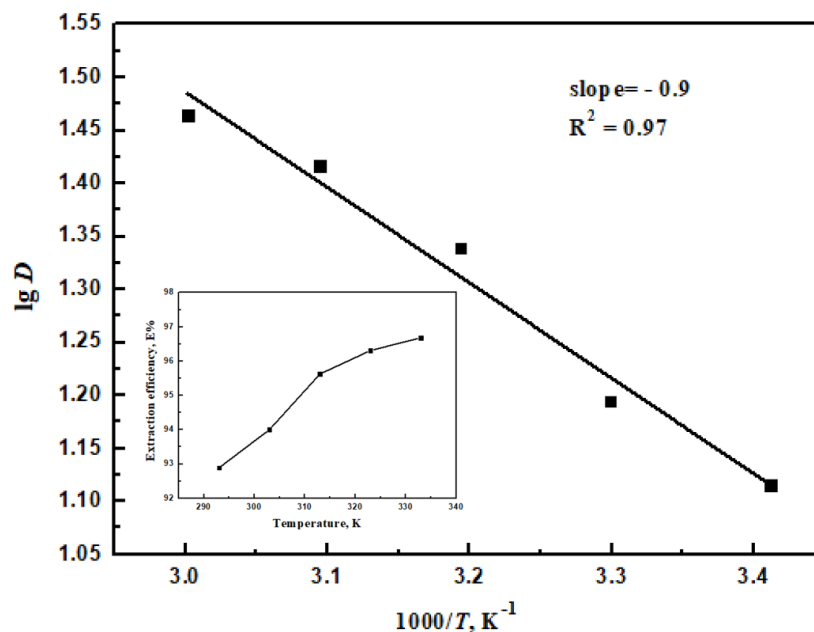
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Fig. 10. Effect of temperature on boron extraction. [TMPD] = 0.4 mol/L; pH_{ini} = 4.6; O/A = 1.

3.2 Spectroscopic studies of the organic and aqueous phases

Raman spectroscopy and FTIR spectroscopy can provide specific information on chemical bonds in molecules by detecting the radiation absorption caused by vibrational patterns[30]. Raman is more suitable for studying the structural characteristics of molecules in aqueous solutions. In previous studies, Raman spectroscopy has been used for the characterization of $B(OH)_3$ and $[B(OH)_4]^-$, whose main absorption peaks were assigned as 875 cm^{-1} and 750 cm^{-1}, respectively[33,34]. Therefore, following aqueous phase trials using pH values ranging from 1 to 7 and a H_3BO_3 concentration of 0.2 mol/L (dissolved in saturated magnesium chloride solution), Raman spectra of aqueous samples were obtained and presented in Fig. 11. With the increase of pH, the intensity of the absorption peak of H_3BO_3 decreases gradually, and the absorption peak of $[B(OH)_4]^-$increases gradually, indicating that the existing form of boron in aqueous solution was gradually converted from $B(OH)_3$ to $[B(OH)_4]^-$. Then, TMPD/CCl$_4$ extraction system was used to extract these aqueous solutions. The experimental results are shown in Table 3. When pH [?]2, the formation of binary boric acid ester and the release of H$^+$ reduce the pH in the solution. The results of extraction efficiency indicate that $B(OH)_3$ is easier to complex with TMPD, so the extraction efficiency is higher under acidic conditions.

Fig. 11. Raman spectra of boron-containing brine at different pH values.

Table 3. Results of extraction of boron-containing saturated magnesium chloride solution at different pH values using TMPD.

pH of Feed brine	pH of Raffinate	ΔpH	Extraction efficiency, %	Distribution ratio, D
1.04	0.98	-0.06	97.54	39.63
2.01	1.69	-0.32	96.92	31.44
3.04	4.43	1.39	94.84	30.79
3.99	6.41	2.42	91.39	10.61
5.00	7.03	2.03	83.86	5.19

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pH of Feed brine	pH of Raffinate	ΔpH	Extraction efficiency, %	Distribution ratio, D
5.98	7.08	1.10	81.09	4.29
7.03	7.31	0.28	75.59	3.10

FTIR spectroscopy has also been applied to investigate the extraction mechanism. Two different solute solutions were extracted (1. 0.2 mol/L H_3BO_3 dissolved in saturated magnesium chloride; 2. 0.2 mol/L H_3BO_3 dissolved in deionized water), each of which had the same pH and H_3BO_3 concentration. Both extraction tests were carried out under the same operating conditions. The samples of organic and blank organic phases were analyzed by IR respectively, and the results were shown in Fig. 12. It is obvious that the IR spectra of two loaded organic phases are similar, indicating that the extraction complexes in the organic phase is independent of whether $MgCl_2$ is present in the solution. Compared with the blank organic phase, the absorption bands of O-H shifted significantly from 3377 cm^{-1} to 3444 cm^{-1}, but it did not disappear and the intensity had been slightly reduced, indicating the presence of TMPD that did not participate in the reaction. The new absorption peaks observed at 1416 cm^{-1}, 1339 cm^{-1} and 661 cm^{-1} were identified to alcohol O-H, C-O and B-O bonds of the boric acid ester, respectively. We therefore conclude that the O-H groups of the alcohol are complexed with boric acid. The evidence for the extraction complex is similar to the results obtained previously by our group using 2-butyl-1-n-octanol[28]. The results will be helpful to understand the mechanism of the complexation reaction between alcohol extractants and boron.
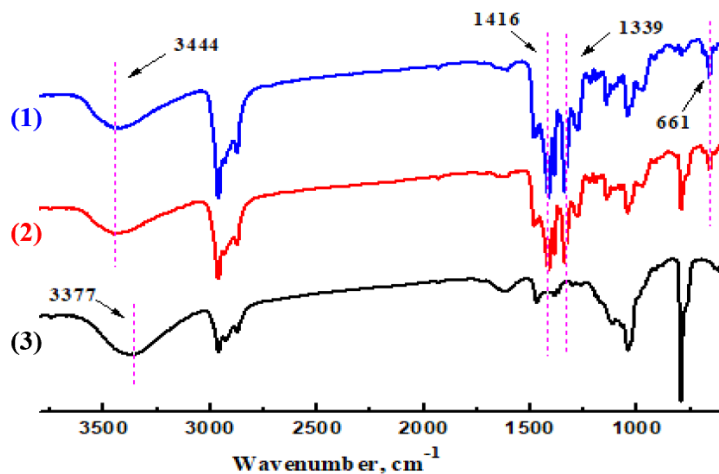

Fig. 12. IR spectra of the organic phases. The organic phase after extraction of (1) H_3BO_3 dissolved in saturated magnesium chloride, (2) H_3BO_3 dissolved in deionized water; (3) The organic phase before extraction.

3.3 Three-stage continuous countercurrent extraction

In order to completely extract H_3BO_3 from brine, we performed an experiment using the three-stage continuous countercurrent extraction (O/A=1) determined by the McCabe-Thiele method (as shown in Fig. 13). SL brine presented in Table 1 was used as aqueous phase. 0.4 mol/L TMPD dissolved in CCl_4 was used as organic phase. The experiment results are listed in Table 4. Finally, the raffinate of 0.0253 g/L H_3BO_3 and the organic containing 12.340 g/L H_3BO_3 were obtained, which corresponds to an extraction efficiency of H_3BO_3 of 99.79%. The results show that the extraction efficiency of H_3BO_3 and distribution ratio are significantly improved in three-stages countercurrent extraction, and boric acid was almost extracted completely.

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Table 4. Comparison of single-stage and three-stage experiment results.

	Concentration of H_3BO_3 in raffinate, g/L	Concentration of H_3BO_3 in organic, g/L	Extraction
Three-stage extraction	0.0253	12.340	99.79
Single-stage extraction	1.692	10.663	86.23

Fig. 13. McCabe–Thiele diagram of boron extraction using TMPD.

3.4 Study of stripping process

Boron-loaded organics were stripped by hydrochloric acid, deionized water and different concentrations of sodium hydroxide solutions at a constant O/A of 2/1, respectively. As shown in Table 5, it is evident that the stripping efficiency of boron by NaOH is significantly higher than that of H_2O and HCl, which can indicate that the complex formed by boron and 1,3-diol (TMPD) is more stable than that formed by monohydric alcohol. The stripping efficiency of H_3BO_3 increased with the increasing of NaOH concentration. however, emulsification occurs when the NaOH concentration is greater than 0.4 mol/L, which is not conducive to phase separation, and the stripping efficiency decreases when it continues to increase to 0.6 mol/L. Therefore, the concentration of the stripping agent is selected to be 0.4 mol/L, which can achieve a good stripping effect while avoiding the phenomenon of emulsification.

Table 5. Results of stripping H_3BO_3 with different stripping agents

Stripping agent	Concentration of stripping agent, mol/L	Phase ratio, O/A	Concentration of H_3BO_3, mol/L	Concen
			Stripping liquor	Strippe
HCl	0.20	2/1	0.0408	0.171
H_2O	—	2/1	0.0240	0.180
NaOH	0.10	2/1	0.0928	0.145
	0.20	2/1	0.164	0.109
	0.30	2/1	0.231	0.0758
	0.40	2/1	0.303	0.041
	0.50	2/1	0.381	0.0008
	0.60	2/1	0.372	0.0051

3.5 Multi-stage countercurrent process

As shown in Fig. 14, a five-stage extraction and stripping process experiment was performed in separating funnels. 0.4 mol/L TMPD dissolved in CCl_4 was used as organic phase, and filtered brine (presented in Table 1) as feed solution. The phase ratios (O/A) of the extraction and stripping sections were 1/1 and 2/1, respectively. The organic phase is recycled throughout the extraction process. The whole extraction process was performed 25 cycles until the extraction equilibrium became stable. Table 6 showed the main components of the stripping solution samples which were obtained after the system was stabilized. It can be seen that the main impurity ion in the stripping liquor is Mg^{2+}, and the concentration is less than 20 mg/L, while the concentration of other impurity ions is very low. The boron-rich solution obtained can be used for the production of high-purity borax or boric acid products. The results indicated that TMPD is a highly selective extractant for boron extraction. The results of extraction and stripping efficiency are shown in Fig. 15. The results showed that the overall extraction efficiency of boric acid was 97.12%, and the stripping efficiency was 88.98%. It can be seen that the stripping efficiency is not ideal, because a slight emulsification occasionally occurs in the stripping section during the experiment. Although the phase separation is not affected, it has a negative effect on mass transfer, which makes the loaded boron organic phase cannot be

stripped completely, resulting in a decreasing trend of extraction efficiency. The emulsification phenomenon did not occur in single-stage experiments, but appeared in whole extraction process experiments, which also illustrates the importance of multi-stage countercurrent experiments to verify the stability and feasibility of the process.
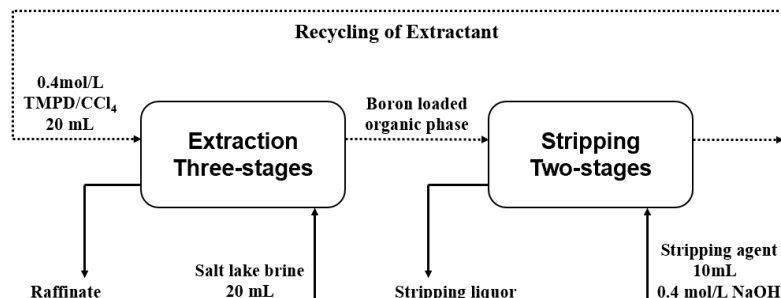

Fig. 14. The flowchart of five-stage extraction and stripping process experiments.

Table 6. Composition of Stripping Solutions

Samples	Concentration of H_3BO_3 (g/L)	Ions Conc. (mg/L)	Ions Conc. (mg/L)	Ions Conc. (mg/L)	Ions Conc. (m
		Li^+	Mg^{2+}	Ca^{2+}	K^+
Str 1	21.73	0.736	13.368	0.040	5.312
Str 2	21.49	0.984	17.686	0.046	4.614

Fig. 15. Results of five-stage countercurrent extraction and stripping experiments with 25 cycles.

4. Conclusions

The extraction of boron using TMPD dissolved in carbon tetrachloride was systematically investigated. The effects of extraction parameters were obtained by varying the pH of feed brine, the concentrations of TMPD and H_3BO_3,and the phase ratio (O/A). The suitable pH range of the TMPD/CCl$_4$ extraction system is [?]7. Logarithm linear regression revealed that 1or 2 equivalent of TMPD were complexed with a single H_3BO_3 molecule, the formation of which was connected with the concentration ratio of TMPD/H_3BO_3. The addition of magnesium chloride showed two opposite effects on the boron extraction, and the lower the pH value, the more promotion effect on boron extraction obviously. The values of ΔH and $\Delta \Gamma$ obtained from the temperature dependence data of extraction efficiency revealed that the extraction process is endothermic and spontaneous. Results from Raman spectra indicated that $B(OH)_3$ was gradually converted to $[B(OH)_4]^-$ as the pH of the solution increased, and $B(OH)_3$ was more easily complexed with TMPD, following which the FTIR spectra was used to analyze the organic phase loaded with boron, the results of which indicated that the O-H groups of the extractant molecule were complexed with boron. On the basis of optimizing the extraction and stripping process, the multi-stage extraction experiments were carried out in the separation funnels, and the experimental results showed that the overall extraction efficiency of boric acid was 97.12%, and the stripping efficiency was 88.98%. This study provides a route to extract boron from the salt lakes brine without acidification. However, the feasibility of this extraction process still requires further investigations.

Acknowledgments

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