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Recovery of boric acid from salt lake brines by solvent extraction with 2-butyl-1-*n*-octanol

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ABSTRACT

A systematic investigation was conducted on the extraction of boric acid from salt lake brine using 2-butyl-1-*n*-octanol dissolved in sulfonated kerosene. The extraction parameters, including the concentration of extractant, phase ratio and pH value of the brine, were optimized. The salting-out effects of the extraction process were investigated in the presence of $AlCl_3$, $MgCl_2$ and NaCl, and an empirical equation was subsequently proposed. The positive salting-out effects were observed on the extraction of boric acid in the order of $AlCl_3 > MgCl_2 > NaCl$. Thermodynamic modeling results indicate that the extraction process is exothermic. To evaluate the feasibility of the process, a multi-stage countercurrent extraction and stripping process was performed under the optimized operating conditions. The results showed an overall boric acid extraction efficiency of 99.35% and a stripping efficiency of 99.63%, and the overall boric acid recovery and the purity of the stripping solution both exceeded 98%. The results of this study reveal a potential industrial application of the boric acid extraction process.

1. Introduction

Boron (B) is an important basic raw material for various industries, including the glass, agricultural, ceramic and textile industries (Lü et al., 2014; Ucar and Yargan, 2009). Boric acid (H_3BO_3), the major natural form or raw material of boron, is generally refined from borate minerals and brines (Kistler and Helvaci, 1994). For example, alkali and alkaline earth metal borates (such as borax, colemanite, ulexite or kernite) react with strong acids to yield boric acid, but the process is expensive, environmentally hazardous and damaging to equipment due to the involvement of strong acids (Mergen et al., 2003). There is an abundance of boron mineral resources reserved in the brine in the Qinghai salt lake. For the extraction of boric acid from the salt lake, the main processes that have been studied are (1) membrane filtration, (2) electrodialysis, (3) reverse osmosis, (4) adsorption, (5) chemical precipitation and (6) solvent extraction (Liu et al., 2009; Öztürk and Köse, 2008; Cengeloglu et al., 2008; Melnik et al., 1999; Tu et al., 2010). Of these, solvent extraction is the most efficient separation method for extracting boric acid from the salt lake brine. Certain alcohols, such as monohydric alcohol (Vinogradov, 1962; Hejda and Jedináková, 1983), dibasic alcohol (Egneus and Uppström, 1973; Karakaplan et al., 2004; Mohapatra et al., 2008; Tural et al., 2014) and mixed alcohols (Ayers et al., 1981; Neikova et al., 1979), have excellent properties for extracting boric acid from the brine.

Among aliphatic alcohols, the applications of aliphatic monohydric alcohol, i.e., 2-ethylhexanol, and dibasic alcohol, i.e., 2-ethyl-1,3-hexanediol, have been investigated systematically. Dibasic alcohol has demonstrated a high extraction efficiency since it can form relatively stable six-membered cyclic borate compounds with boric acid (Bachelier and Verchere, 1995). Schiappa et al. (1970) reported that 1,3-diols (such as 2-ethyl-1,3-hexanediol, 3-methyl-2,4-heptanediol, 2,2,4-trimethyl-pentanediol, 2-butyl-2-ethyl-1,3-propanediol, 2-methyl-2-nonyl-1,3-propanediol, 2,2-diaryl-1,3-propanediol, etc.) showed excellent extraction properties for boric acid in brine with high concentrations of calcium and magnesium, with a distribution coefficient of > 10 and a single-stage extraction efficiency of > 90%. Hejda and Jedináková (1983) and Hejda and Jedináková (1988) separated boric acid from radioactive wastes using *n*-hexanol, *n*-octanol, 2-ethylhexanol, *n*-decanol, etc. as extractants. The results showed that 2-ethylhexanol was superior to other alcohols, and the boron distribution

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coefficient reached 1.37. Zhang et al. (2016) studied the extraction of boron from salt lake brine using 2-ethylhexanol. An eight-stage extraction process, including extraction, scrubbing, and stripping, was proposed, and the results showed an overall boron extraction efficiency of 99.5% with a purity of 95.5%. However, the high solubility of 2-ethylhexanol (up to 1 g/L in water) limited further industrial applications (Amidon et al., 1974). Compared to monohydric alcohols, dibasic alcohols have shown a higher extraction efficiency for boron and lower solubility in water, but alkaline solutions are needed to strip the boron completely from the loaded organic phase (Hirata, 2005). A novel monohydric alcohol, 2-butyl-1-n-octanol, which exhibits extremely low water solubility (0.01 g/L at 296.15 K), was introduced to extract boric acid from salt lake brine.

In this study, 2-butyl-1-*n*-octanol was first used as an extractant for removing boric acid from salt lake brine. The extraction experiments were conducted under different conditions to determine the optimal parameters. Thermodynamic analysis was used to determine the thermodynamic parameters of the boric acid extraction reaction. Stripping of boric acid from the loaded organic phase was investigated along with the re-usability of the organic phase. The results of this research indicated that the liquid–liquid extraction process of recovering boric acid from salt lake brine has potential on an industrial scale.

1.1. Experimental procedure

Aqueous solutions were prepared by filtering acidified West Taijinaier salt lake brine. The main element concentrations and properties are listed in Table 1. Separately, simulated brine was prepared by dissolving boric acid and salts in deionized water for the experiments pertaining to salting-out effects. Organic solutions were prepared by dissolving 2-butyl-1-*n*-octanol in sulfonated kerosene at different concentrations. Equilibrium experiments were conducted in a separation funnel with polytetrafluoroethylene stopcock. The mixtures containing different volumes of aqueous and organic phases were mechanically shaken at a frequency of 300 rpm for 15 min and then left to settle for approximately 30 min. Organic and aqueous phase samples were then taken from the separation funnel for solute concentration analysis. All extraction experiments were carried out at room temperature (293 ± 1 K), apart from the experiments at variable temperatures for the determination of thermodynamic parameters, where the temperature was varied over the range of 293–333 K. The pH of the aqueous solution was adjusted by small amounts of hydrochloric acid and sodium hydroxide. The reproducibility of results was checked by repeating the experiments at least twice, and the standard deviations were found to be within ± 2%.

2. Experiment

2.1. Reagents

All the reagents used in this study were of analytical grade and were used without further purification. The 2-butyl-1-*n*-octanol ($C_{12}H_{26}O$, M_w = 186.34 Da., ρ = 0.836 g/cm^3, purity > 98%) was supplied by the TCI (Shanghai) Chemical Industry Development Co. Sulfonated kerosene was bought from a local market. All inorganic compounds were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water was used throughout the experiments.

Table 1
Main composition and properties of the salt lake brine.

ρ (g/cm^3)	pH	Ion concentration (g/L)					
		H_3BO_3	Li^+	Na^+	Mg^{2+}	Cl^-	SO_4^{2-}
1.36	1.30	14.84	1.96	1.46	113.76	330.03	30.89

2.2. Analysis

The boric acid in the aqueous phase was titrated with standard 0.05 mol/L sodium hydroxide, using phenolphthalein as the indicator. For aqueous phases, the sample was diluted with water containing D-mannitol to increase the strength of the boric acid (Celeste et al., 2012). The boric acid in the organic phase was analyzed after being stripped completely into the aqueous phase. A mass balance of boron in the aqueous and organic phases confirmed the analysis was accurate. The concentration of chloride was titrated with standard 0.05 mol/L $Hg(NO_3)_2$. All titrations were carried out at least twice. The concentrations of the cations and sulfate in the aqueous samples were analyzed using Inductively Coupled Plasma Atomic Emission Spectrometry (ICAP6500DUO, Thermo, US). FTIR spectra were measured in the 4000–450 cm^{-1} range with a Thermo Nicolet Corporation 670 Spectrometer.

The extraction efficiency (E) and the distribution ratio (D) were calculated according to the following equations:

$$E = \frac{V_{organic} * [B]_{organic}}{V_{aqueous} * [B]_{aqueous} + V_{organic} * [B]_{organic}} * 100\% \quad (1)$$

$$D = \frac{[B]_{organic}}{[B]_{aqueous}} \quad (2)$$

where $[B]_{organic}$ is the equilibrated concentration of boron in organic phase; $[B]_{aqueous}$ is the equilibrated concentration of boron in aqueous phase; and $V_{organic}$ and $V_{aqueous}$ represent the volume of organic and aqueous phases, respectively.

3. Results and discussion

3.1. Determination of the extraction parameters

3.1.1. Effect of 2-butyl-1-n-octanol concentration

The extraction effects of boric acid by the 2-butyl-1-*n*-octanol/kerosene system with varying concentrations of 2-butyl-1-*n*-octanol were studied. The 2-butyl-1-*n*-octanol concentration was varied over the range 0.5–4.5 mol/L, with approximately 4.5 mol/L being the concentration of pure 2-butyl-1-*n*-octanol. As shown in Fig. 1, the increasing 2-butyl-1-*n*-octanol concentration showed a positive effect on the boric acid extraction performance. The maximum extraction efficiency and distribution ratio of H_3BO_3 reached 94.7% and 17.9, respectively, when the 2-butyl-1-*n*-octanol concentration was 3.5 mol/L. The extraction efficiency remained almost unchanged within the margin of error after 3.5 mol/L. According to Fig. 2, the viscosity of the

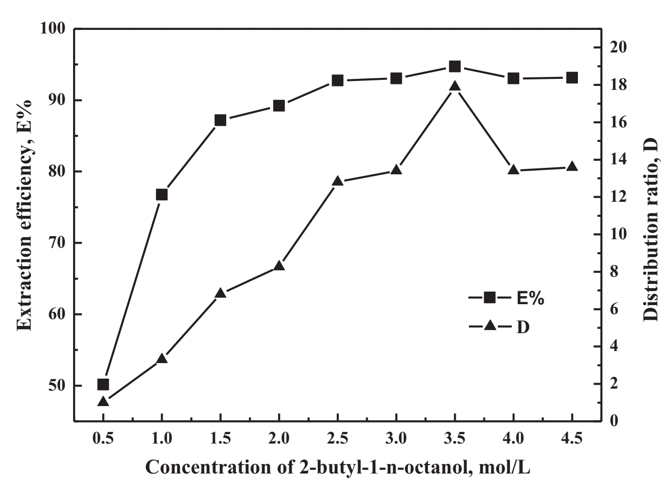

Fig. 1. Variation in distribution ratio and extraction efficiency with respect to the concentration of 2-butyl-1-*n*-octanol; O/A = 1; *T* = 293 K; pH = 1.3.