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Extraction of boron from salt lake brine using 2-ethylhexanol

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ABSTRACT

A systematic investigation on the extraction of boron from salt lake brine using 2-ethylhexanol as the extractant is reported with an emphasis on the extraction thermodynamics and extraction process design in order to obtain high purity boron product. The extraction parameters were optimized with respect to the time of extraction, volume percentage of extractant, phase ratio, and the concentration of magnesium. Logarithm linear regression revealed an average association constant of 0.7 for 2-ethylhexanol and boric acid. Thermodynamic modeling results indicate that the association is an exothermic, enthalpy driven process. A three-stage countercurrent extraction and stripping was designed in order to assess the process feasibility. Results showed an overall boron extraction efficiency of 99.5% with a purity of 95.5%. In addition, attempts were also made on improving the product purity with a two-stage washing step. These results indicate the application potential of present extraction process.

1. Introduction

Boron (B) is an essential micronutrient for animals and plants. In addition, its many special properties, such as flame retardance, heat and wear resistance, high rigidity, and high strength (Ivanovskii, 1997; Kistler and Helvaci, 1994), render it an important basic raw material for various industries. Boron is widely present in solid boron ore and liquid ore (Kesler et al., 2012; Wei et al., 2014), mainly in the form of boric or borate salts (Xu and Jiang, 2008). Current boron extraction is mostly achieved by refinement of boron ore, i.e. colemanite and borax (Nishihama et al., 2013). The extraction of boron from salt lake brine remains a great challenge although the concentration of boron is of significant interest. For example, in the Qinghai salt lake located in the northwest of China, the brine contains various inorganic ions, such as K, Mg, Na, and Ca, mainly in the chloride form in addition to B. Some of the elements are highly concentrated, for example magnesium (up to 250 g/L). Currently, potassium chloride has been successfully exploited as a fertilizer, leaving boron and lithium unexplored (Ma, 2000; Li et al., 2009a). Successful utilization of boron and other valuable chemical resources has a great added value to the regional economic development (Du, 2014). However, so far there have been only few reports in Chinese on the extraction of boron from salt lake brine. The extraction of boron from high salinity sources and process efficiency remain largely unexplored.

In aqueous solutions, boron may exist as boric acid [$B(OH)_3$] or borate ion [$B(OH)_4^-$] depending upon the solution pH (Bachelier and Verchere, 1995; Badruk et al., 1999). To extract boron from the salt lake brine, several separation methodologies, such as chemical precipitation (Itakura et al., 2005), adsorption (Nishihama et al., 2013; Ooi et al., 1996; Yan and Yi, 2010), ion exchange (Öztürk and Köse, 2008; Yan et al., 2008; Köse and Öztürk, 2008), solvent extraction (Brown and Sanderson; Folkestad et al.,; Foster et al.,; Grinstead, 1972; Tsuboi et al., 1990), reverse osmosis (Cengeloglu et al., 2008; Yavuz et al., 2013a, b), and electrodialysis (Melnik et al., 1999), have been investigated. Chemical precipitation requires a large quantity of hydroxides, which is not only costly but also results in a large amount of chemical wastes. Ion exchange requires frequent regeneration of the resins, which ends up with a large amount of wastewater. Electrodialysis is in general of low selectivity, expensive, and energy-intensive. Furthermore, reverse osmosis is practically not sustainable due to scaling problems and blockage of the membrane caused by the precipitation of inorganic chemicals. Solvent extraction remains the most promising and highly efficient separation technology for extraction of boron from the complicated salt lake brine. Certain alcohols, such as monohydric alcohol (Vinogradov, 1962; Brown and Sanderson, 1978a; Vinogradov et al., 2001), dibasic alcohol (Brown and Sanderson, 1978b; Shvarts et al., 1995; Svares et al., 1983) and mixed alcohols (Lv et al., 2012; Ayers et al., 1981), can associate with boric acid, which makes the extraction possible. However, the extraction of boron from salt lake brine using monohydric alcohol like 2-ethylhexanol has not been systematically investigated, and the whole process of obtaining high purity boron from salt lake brine has not been reported either. Dibasic alcohol has shown a higher extraction efficiency of 95%, but alkaline solutions

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are needed to strip the boron from the organic phase, and the product purity will be dubious because of the contamination by NaOH. Extraction of boron from brine which has a lower concentration of other ions, such as lithium and magnesium after boric acid flotation using A1416 has been reported with a total recovery rate of 83.8% and a product purity of 99.67% with a three-stage extraction and four-stage stripping. However, the extraction of boron from high salinity salt lake brine needs further systematic investigation where an appropriate process is still not available.

In this paper, a low cost extractant 2-ethylhexanol was adopted to extract boron from brine sources taken from East Taijinaier salt lake. The extraction thermodynamics is systematically investigated, and the extraction reaction mechanism proposed. The process parameters for liquid–liquid extraction are investigated for an optimal extraction effect. Stripping of boron from the organic phase using various stripping solution is carried out in order to assess the feasibility of solvent extraction of boron. Results of this research may pave a solid theoretical and technical basis for next step piloting work.

2. Experimental section

2.1. Materials

2-Ethylhexanol ($C_8H_{18}O$, $M_w = 130.23$ Da., $\rho = 0.835$ g/cm^3, purity > 98%) and boric acid (H_3BO_3, $M_w = 61.83$, purity > 99.8%) were supplied by Sinopharm Chemical Reagent Co., Ltd., Sulfonated kerosene (0.790–0.825 g/cm^3) as the diluent was provided by Nanjing Huizhiyuan Petrochem Co. Ltd. Deionized water was used throughout the experiments.

2.2. Liquid–liquid extraction

All liquid–liquid extraction experiments were conducted using separation funnels (150-mL). Both single-stage extraction and multi-stage extraction were investigated as detailed below.

2.2.1. Single-stage extraction

The feed brine (Aqueous, abbreviated as *A phase*) and extractant (Organic phase, abbreviated as *O phase*) were added into the funnel at a certain ratio; vigorous mixing of the O/A phases was conducted for at least 5 min; a 30 min time was allowed for the phase separation. Aqueous and organic phases were sampled for analysis to ensure that the time was sufficient for mixing and phase separation.

2.2.2. Multi-stage extraction

Multi-stage extraction was designed to simulate a countercurrent extraction process with separation funnels as shown in Fig. 1 (Liu et al., 2015; Türkay and Civelekoğlu, 1991). The feed brine was introduced from left side, and the organic phase was added from right side. A countercurrent extraction process was realized.

Fig. 1 shows a scheme of a multi-stage countercurrent extraction process. Each circle represents a batch shake-out. The procedure consisted of repeated introduction of feed (F) and fresh extractant (S) into a series of extraction stages, plus withdrawal of extract and raffinate phases. The overall result was actually continuous, not batch, although feed and extractant were introduced intermittently. After a number of cycles of introducing feed and extractant, extracting, and discharging, the systems approached a steady-state. The liquid flow resembles the streams flow in a countercurrent continuous extraction.

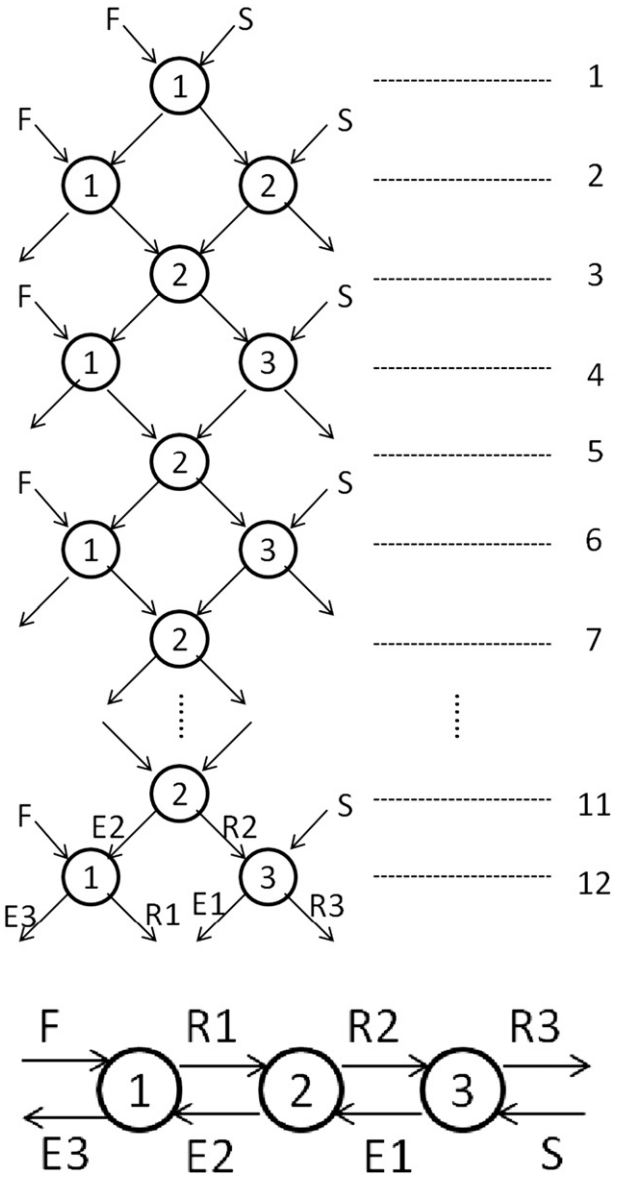

Fig. 1. Batch simulation of three-stage continuous countercurrent extraction. The circle with numbers stands for single-stage extraction, and the number in circle represents serial number. Arrows indicates the flow of the liquid. F: feed; S: fresh extractant; E: organic phase loaded with boron after extraction; R: raffinate.

2.3. Analysis

The concentration of the cations in the aqueous samples was analyzed using an Inductively Coupled Plasma Atomic Emission Spectrometry (ICPE-9000, Shimadzu, Japan). The boron in the organic phase was analyzed after being stripped completely into an aqueous phase. A mass balance of boron in the aqueous and organic phase confirmed the analysis was accurate (deviation <5%). The standard deviation of the ICP measurement for triple samples was <1%. Compared to the commonly used method for measuring the concentration of boron, the precision of ICP is higher (del Mar de la Fuente García-Soto and Muñoz Camacho, 2005). The chlorine ion was analyzed by high performance liquid chromatography using ion selectively column (LC-20A, Shimadzu, Japan). The interfacial tensions were measured by a contact angle goniometer (Maist Drop Meter A-100P) equipped with a high speed CCD camera. The viscosities were measured by a viscometer (DV-II + Pro, Brookfield).