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Recovery of Boric Acid from Wastewater by Solvent Extraction

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ABSTRACT

An extraction system for the recovery of boric acid using 2-butyl-2-ethyl-1,3-propanediol (BEPD) as an extractant was studied. Loss of the extractant to the aqueous solution was lowered by using 2-ethylhexanol as a diluent. The extraction equilibrium of boric acid with BEPD was clarified, and the equilibrium constants for various diluents were determined. Furthermore, continuous operation for the recovery of boric acid using mixer-settlers for extraction and stripping was successfully conducted during 100 hours.

Key Words. Boron; Solvent extraction; Aliphatic diol; Wastewater

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INTRODUCTION

A high concentration of boron is present in the wastewater from a boron mine and from the desulfurizing equipment in steam power stations using coal. It is known that although a low level of boron is essential for vegetation, it is toxic at concentrations greater than about 5 mg/L (1). Therefore, the concentration of boron in wastewater must be reduced to a low level. Up to now, a chelating resin with the *N*-methyl(polyhydroxyhexyl)amino group has been used for selective boron recovery (2). Recently, a combined process of adsorption and solvent extraction techniques has become attractive as a recovery process for boron because it can treat and purify large quantities of wastewater easily (3).

Boron exists as boric acid or borate in an aqueous solution. According to Brown and Sanderson (4), extractants for boron are classified into three groups: (a) extracts of boric acid without any reactions (physical extraction); (b) extracts of boric acid accompanying a reaction which forms a neutral ester; (c) extracts of boric acid accompanying a reaction with tetrahydroxy borate to form a borate salt complex.

In the case of physical extraction, high extractability is not attainable. The extractants belonging to groups (b) and (c) are suitable for extracting boron from acidic and alkaline solutions (4), respectively. Since the eluate from a column packed with the chelating resin mentioned above is acidic (3), aliphatic 1,3-diols belonging to group (b) are suitable for the extractants in this work.

Among aliphatic 1,3-diols, it was reported that 1,3-diols with 8 or 9 carbon atoms (5) have a maximum extraction capacity. 2-Ethyl-1,3-hexanediol (EHD) was therefore used for the recovery of boron from the coal fly ash (3) and geothermal water (6). However, because the solubility of EHD in an aqueous solution is high (4), the recovery of boron from wastewater using EHD is practically impossible. In the present study an extraction system for boric acid using 2-butyl-2-ethyl-1,3-propanediol (BEPD) was studied because of its practical use. It was expected that the solubility of BEPD in an aqueous solution would be lower than that of EHD because of the increase in the carbon number from 8 to 9. Furthermore, a continuous operation using mixer-settlers for extraction and stripping was carried out.

EXPERIMENTAL

Reagents

All the reagents were of reagent or higher grade and were purchased from Nakalai Tesque or Wako Pure Chemicals except for reagent-grade

BEPD which was from Tokyo Chemicals Ind. All reagents were used without further purification. All aqueous solutions were prepared with distilled and deionized water.

Distribution of Diol Extractants

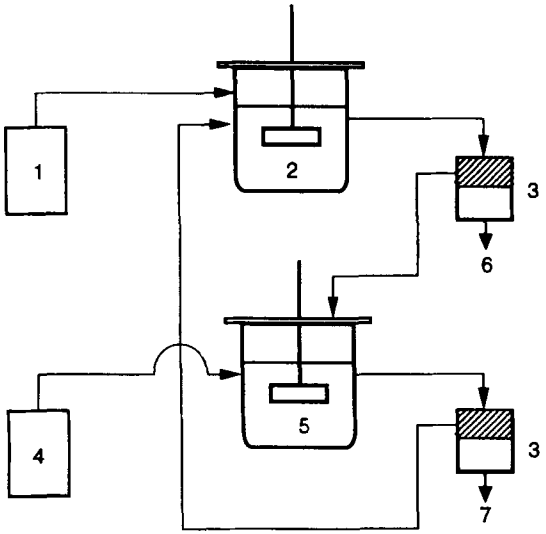
Distribution equilibria of the diol extractants EHD and BEPD between organic and aqueous solutions were examined. The aqueous solution was prepared without pH adjustment. The organic solutions were prepared by dissolving the extractant in various organic solvents. Equal volumes (20 cm^3) of the aqueous and organic phases were taken into a flask, and this was shaken in a constant-temperature bath (298 K). After equilibration, the concentrations of BEPD and EHD in the aqueous and organic solutions were determined by gas chromatography (Shimadzu GC-8AIF, FID detector, column; 10% PEG 6000 on Shimalite TPA, column temperature, 453 K; injection temperature, 553 K; carrier gas, N_2).

Solvent Extraction of Boric Acid

The aqueous solution was prepared by dissolving boric acid. The pH of the aqueous solution was adjusted to 6 by a buffer solution with a concentration of 0.1 mol/dm^3 $NaOH–Na_2HPO_4$. The organic solutions were prepared by dissolving the extractant in various organic solvents. Equal volumes (20 cm^3) of the aqueous and organic phases were taken into a flask, and this was shaken in a constant temperature bath (298 K). After equilibration, the concentration of boric acid in the aqueous phase was measured by spectrophotometric determination with Azomethine H (7). Stripping of boron from the organic phase was conducted using a sodium hydroxide aqueous solution as the stripping agent.

Continuous Operation Using Mixer-Settlers

Continuous operation for the recovery of boron was carried out using two mixer-settlers for extraction and stripping at 298 K as shown in Fig. 1. The mixer was a stirred glass cell of 10 cm inner diameter and 15 cm depth. The vessel is fitted with four stainless-steel baffles. Stirring was carried out using a turbine impeller of 5.3 cm diameter, having six flat blades, connected to a speed controller. The settler was a 300-mL Erlenmeyer flask connected with two glass tubes for effluents. The organic solution was circulated between the two mixer-settlers. The experimental conditions are listed in Table 1. The feed aqueous solution was prepared without pH adjustment. The concentrations of boric acid in the aqueous feed and effluent, and that of BEPD in the circulating organic solution, were determined by the above methods at proper time interval.



1. Feed solution 2. Mixer for extraction 3.Settler
4. Stripping solution 5. Mixer for stripping 6. Raffinate
7. Strip solution

FIG. 1 Experimental apparatus for continuous operation.

TABLE 1
Experimental Conditions for Continuous Operation

Feed aqueous solution:	
Initial concentration of boric acid	0.03 mol/dm^3
Flow rate	10 mL/min
Organic solution:	
Initial concentration of BEPD	0.25, 0.53, 1.1 mol/dm^3
Circulation rate	10 mL/min
Stripping aqueous solution:	
Initial concentration of NaOH	0.5 mol/dm^3
Flow rate	10 mL/min
Stirring rate	400 rpm
Temperature	298 K

RESULTS AND DISCUSSION

Extraction System of Boric Acid

Figure 2 shows the extent of extraction of boric acid with EHD or BEPD, E, in kerosene. In the figure the repetitive times indicate the number of repetitions for the extraction and stripping operation using the same organic solution in a batch experiment. The borate complex in the organic solution was completely stripped by 0.5 mol/dm^3 NaOH solution in each step. As is evident from Fig. 2, E was drastically decreased with repetitions of extraction and stripping in the case of EHD. In the case of BEPD, the extent of decrease was smaller than that of EHD, but by the fourth time E approached zero. This were caused by loss of the extractant to the aqueous solution. Therefore, the effect of diluent on the distributions of EHD and BEPD between the organic and aqueous phases was examined. Table 2 lists the distribution ratio, $D_{R(OH)_2}$ (= concentration in aqueous phase/concentration in organic phase), of EHD and BEPD between the organic and aqueous solutions for an initial concentration of 1 mol/dm^3 and equal phase volumes. Table 2 shows that the BEPD–2-ethylhexanol system gave the smallest $D_{R(OH)_2}$. The reason for this will be discussed later. We decided to use the BEPD–2-ethylhexanol system for the continuous operation.

Extraction Equilibrium of Boric Acid with BEPD

Figure 3 shows the relation between the distribution ratio of boric acid, D_B, and BEPD concentration, [R(OH)$_2$], in various diluents. The order

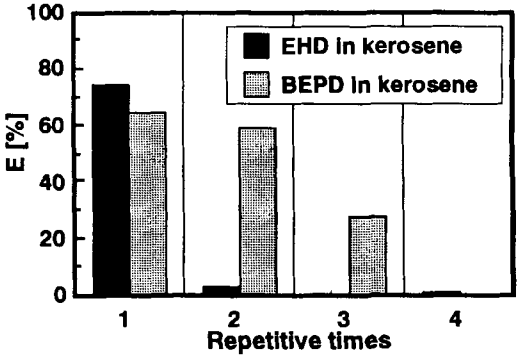


FIG. 2 Effect of repetitive operation on extent of extraction of boric acid with EHD and BEPD.

TABLE 2
Distribution Ratio of EHD and BEPD between Organic and Aqueous Phases[a]

Solvent	EHD	BEPD
Isooctane	0.263	Formation of third phase
Hexane	0.203	Formation of third phase
Toluene	0.147	0.009
Oleyl alcohol	0.084	Emulsification
Dodecyl alcohol	0.063	Emulsification
2-Ethylhexanol	0.026	<0.001

[a] Initial concentration of extractant = 1 mol/dm^3. Volume ratio of aqueous to organic solutions = 1.

of the distribution ratio of boric acid in a high BEPD concentration range was as follows: toluene > kerosene > hexane > 2-ethylhexanol. Although 2-ethylhexanol gave the lowest extractability, the difference in extractability among the diluents investigated was relatively small. Therefore, it was decided that the BEPD–2-ethylhexanol system is suitable for practical use from the viewpoint of loss of extractant to the aqueous solution. Because 2-ethylhexanol causes a large decrease in the activity of BEPD compared with the other diluents, the distribution of BEPD to the aqueous

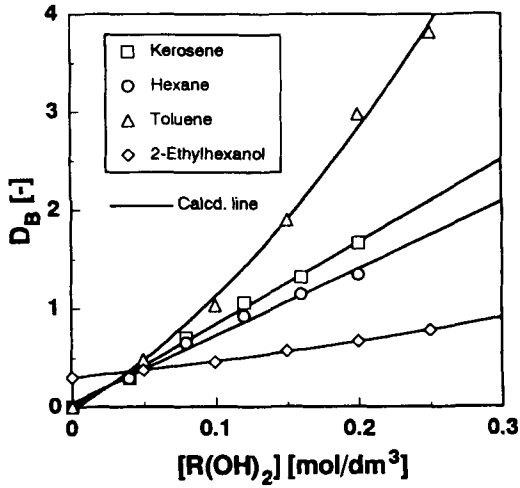


FIG. 3 Relation between distribution ratio of boric acid and BEPD concentration.

solution and the extent of extraction of boric acid with BEPD are considered to be small. This may be due to the strong hydrogen bonding between alcohols, 2-ethylhexanol, and BEPD (8). The apparent dependency of log D_B on log[$R(OH)_2$] was about 1–1.2, which suggests that extraction has the following reaction steps (6, 9, 10):

$$B(OH)_{3,aq} \rightleftharpoons B(OH)_{3,org} \qquad K_D \tag{1}$$

$$B(OH)_{3,aq} + R(OH)_2 \rightleftharpoons HBO_3R + 2H_2O \qquad K_1 \tag{2}$$

$$B(OH)_{3,aq} + 2R(OH)_2 \rightleftharpoons HBO_4R_2 + 3H_2O \qquad K_2 \tag{3}$$

where K_D, K_1, and K_2 are the extraction equilibrium constants of Eqs. (1) to (3) based on the concentration, respectively.

From the above equilibria, in the pH range less than pK_a (= 9) the distribution ratio is approximately expressed as follows:

$$D_B = K_D + K_1[R(OH)_2] + K_2[R(OH)_2]^2 \tag{4}$$

K_D, K_1, and K_2 were determined by a nonlinear parameter estimating method. Table 3 lists the values obtained for each solvent. The solid lines in Fig. 3 were calculated according to Eq. (4) by using these constants.

Continuous Operation Using Mixer-Settlers

Continuous operation for the recovery of boric acid with BEPD in 2-ethylhexanol was carried out by using the mixer-settlers shown in Fig. 1. Figures 4 and 5 show the time courses of the extent of extraction, E, and the BEPD concentration in 2-ethylhexanol for various initial BEPD concentrations. Continuous operation was successfully conducted during about 100 hours. No problems of emulsification and phase separation in the settlers was encountered during continuous operation. From these figures, E and the BEPD concentration was found to gradually decrease with time due to the loss of extractant to the aqueous solution. Such a loss is inevitable unless the feed and stripping solution are presaturated

TABLE 3
Extraction Equilibrium Constants of Boric Acid with BEPD

Solvent	K_D (—)	K_1 (dm³/mol)	K_2 (dm⁶/mol²)
Toluene	0	8.7	28
Kerosene	0	8.4	0
Hexane	0	6.8	0
2-Ethylhexanol	0.3	1.5	1.9

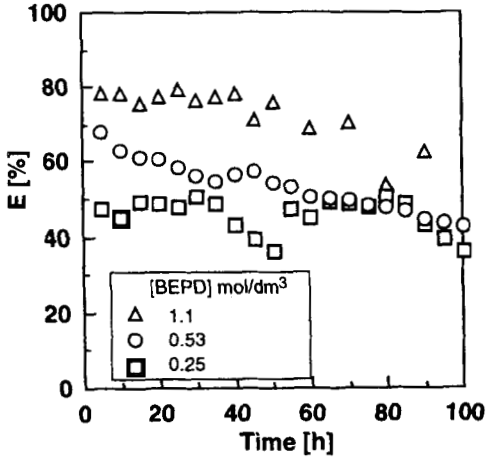


FIG. 4 Time courses of extent of extraction of boric acid in continuous extraction using mixer-settlers.

with the extractant solution. It is necessary for this solvent extraction process to be examined by an economic analysis including the loss of extractant and treatment of the organic component solubilized in the aqueous media.

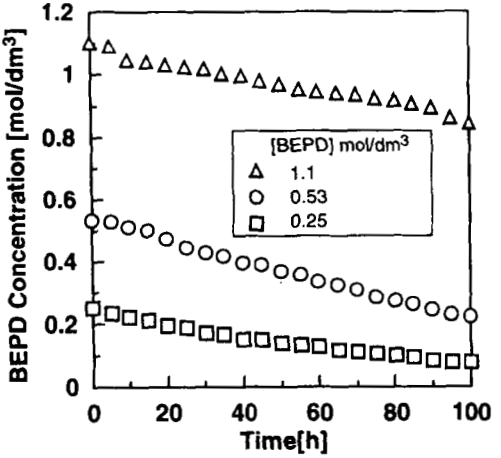


FIG. 5 Time courses of BEPD concentration in continuous extraction using mixer-settlers.

CONCLUSION

An extraction system for the recovery of boric acid was studied from the viewpoint of practical use by using 2-butyl-2-ethyl-1,3-propanediol (BEPD) as the extractant. Loss of the extractant to the aqueous solution was lowered by using 2-ethylhexanol as a diluent. The extraction equilibria of boric acid with BEPD were clarified, and the equilibrium constants were determined for various diluents. Based on the loss of the extractant to the aqueous solution and extractability, the BEPD/2-ethylhexanol system was optimum for the recovery of boric acid from wastewater. Continuous operation for the recovery of boric acid with BEPD in 2-ethylhexanol using mixer-settlers for the extraction and stripping was successfully conducted during 100 hours. The economic feasibility of this extraction process depends on treatment cost of the wastewater, including trace contaminants such as the extractant and diluent.

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