Boron Removal and Recovery from Wastewater by Solvent Extraction with 2-Butyl-2-Ethyl-1,3-Propanediol
On-line Number 1075

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ABSTRACT

Solvent extraction has been known as an appropriate method to remove boron from wastewaters. Diols have been used most intensively for this purpose. In this study, equilibriums of boron extraction and stripping with a 1,3-diol was investigated at various boron and extractant concentrations, and pH values. From the distribution ratio of boron it was obvious that boron extraction was not affected by boron concentration, but it increased with the concentration of 2-butyl-2-ethyl-1,3-propanediol (BEPD), the extractant. In stripping, however, it was clear that the distribution ratio of boron decreased with boron concentration, and a stronger effect of BEPD concentration on stripping than on extraction was observed. From the data of the pH dependence of boron distribution ratio it clarified that boron extraction was intensive in acidic solution but in alkaline solution stripping of boron took place dominantly. The effect of K⁺ ion on boron stripping was also examined, and the result clarified that boron extractability increased with the concentration of K⁺ ion in the stripping phase even at high pH value as 12.5 to prevent stripping.

KEYWORDS
boron, solvent extraction, 1,3-diol, wastewater treatment

INTRODUCTION

Boron is widely distributed throughout the earth at low concentration as borates (boron bonded to oxygen), and it is rarely found in high enough concentration to be commercially significant in exploitable ore bodies (Robert, 2002). Boron is an essential material in many industries so that over 9,000 tones of borates are imported to Japan every year. Because of the environmental problem caused by contaminated water with boron, however, it is also the subject of regulation with permitted discharge concentrations of 10 g/m³ and 230 g/m³ as boron in the non-sea area and sea area, respectively, in Japan. Therefore, it is in need to develop a feasible method for boron removal from wastewaters. Furthermore, it is very helpful to Japanese industry if it is possible to recover boron from wastewaters and to make it a resource. There are many coal-fired thermal power plants in Japan, and relatively concentrated boron is included in the wastewater from them. Solvent extraction has been considered as the most feasible method to remove boron from waters for decades because of low cost and easy treatment, and various diols have been used
most intensively for this purpose (Babcock and Pizer, 1980, Bachelier and Verchere, 1995, Biçak, Gazi, and Bulutcu, 2003, Brown and Sanderson, 1980, Dyrsen, Uppström, and Zangen, 1969 (a), (b), Egneus and Uppström, 1973, Grinstead and Creek, 1969, Hoşgören, et al., 1997, Kahraman, 1995, Paal, 1980, Pizer and Tihal, 1992, 1996, Poslu and Dudeney, 1983, Vinogradov and Tarasova, 1994). In our previous works also, boron extraction with 1,3-diols, BEPD and EHD was carried out to remove boron from hot spring water or the wastewater from a coal-fired thermal power plants (Hano, et al., 1994, Hirata, et al., 2000, Kwon, et al., 2004, Matsumoto, et al., 1997). However, it is rarely reported on boron stripping process needed for the recovery of boron. In this work, equilibriums of boron extraction and stripping were investigated at various concentrations of boron and BEPD and pH values. The effect of K⁺ ion concentration on boron stripping was also examined.

**EXPERIMENTAL**

**Reagents**

All the reagents used in this study were of analytical grade and were used without further purification. All the reagents were purchased from Wako Chemicals Industries, Ltd., Japan.

**Boron Extraction**

Aqueous solutions were prepared by dissolving boric acid in deionized water for boron concentrations of 0.1-0.5 kmol/m³. Organic solutions were prepared by dissolving BEPD in 2-ethylhexanol (EHA) for BEPD concentrations of 0.3-6.2 kmol/m³. Then equal volumes of aqueous and organic solutions were taken into an Erlenmeyer flask, and this was shaken for over 15 hours in a thermostated water bath at 25 °C. The pH was not adjusted at all for the experiments since the pH of aqueous boric acid solution was between 5 and 6.

**Boron Stripping**

The organic solutions after extraction were used as the organic phases for the experiments of boron stripping. The aqueous alkaline solution was prepared by dissolving potassium hydroxide in deionized water for KOH concentration of 1 kmol/m³. The experiment was conducted by the same manner and conditions as used for boron extraction but the flask was stirred for over 15 min. instead shaken.

To examine the effect of pH on boron stripping, the aqueous acidic solution, of which pH was 3, was prepared by adding a drop of sulfuric acid as the aqueous phase for this experiment. The aqueous and organic phases in a beaker were stirred for a while until the equilibrium of the reaction was achieved and the mixed solution was allowed to separate. After separating was completed the samples both of the
aqueous and organic phases were taken. After that concentrated to 5 kmol/m³ KOH solution was added to the beaker to change the pH and the solutions were stirred again. The equilibrium pH values were adjusted from 3 to 14.

For another experiment to examine the effect of K⁺ ion concentration on boron stripping, the aqueous solutions were prepared by dissolving potassium chloride in deionized water for KCl concentrations of 0.04-4.0 kmol/m³. Then the aqueous and organic phases were stirred for over 15 min. and concentrated to 5 kmol/m³ KOH solution was added in the mixed solution to adjust the equilibrium pH to 12.5.

Analysis

After extraction and stripping equilibriums were achieved, the mixed solution was allowed to separate into organic and aqueous phases. The concentration of boron in both aqueous and organic phases was then measured spectrophotometrically by the modified Azomethine H method by which the concentration of boron in the organic phase could be also measured.

RESULTS AND DISCUSSION

Equilibriums of Boron Extraction and Stripping

Boron extraction and stripping were carried out at various initial concentrations, 0.1-0.5 kmol/m³, of boron in the aqueous and organic phases, respectively, and at various initial concentrations, 0.3-6.2 kmol/m³, of BEPD in the organic phase. The initial pH values of the aqueous phase for boron extraction and of the stripping phase for boron stripping were 5-6 and over 14, respectively. The relation between the distribution ratio of boron and the initial concentrations of boron in the aqueous or organic phase is shown in Fig. 1. In extraction, the distribution ratio of boron was almost the same for all concentrations of boron in the aqueous phase and it increased with the initial concentration of BEPD in the organic phase. But the distribution ratio of boron decreased with the initial concentration of boron in the organic phase in stripping and it increased with BEPD concentrations. At BEPD concentration of 0.3 kmol/m³, however, the distribution ratio of boron was constant. In addition, the maximum extractability of boron was around 50 % at 0.3 kmol/m³ BEPD in EHA solution so that the highest concentration of boron in the organic phase was 0.35 kmol/m³ at that BEPD concentration. From these results it was demonstrated that at low BEPD concentration as 0.3 kmol/m³ BEPD in EHA, boron extraction and stripping were under control of EHA which extracted boron by means of a physical action, but they were under control of BEPD which extracted boron by means of a chemical reaction at high BEPD concentrations in alkaline solutions. In Fig. 2, the relation of the distribution ratio of boron and the initial concentration of BEPD in the organic phase is shown. In extraction, the distribution ratio of boron showed a leaner increase with the initial
concentration of BEPD in the organic phase but it increased dreadfully in the case of stripping. From these results, it clarified that boron extraction was not affected by boron concentrations but stripping was, and the effect of BEPD concentrations on boron stripping was much stronger than on extraction. From this fact, it was considered that the mechanisms of boron extraction and stripping with BEPD in EHA were different, and the difference might be explained by the fact that boric acid, which reacts with BEPD to form 1:1 ester, in the acidic media transformed into tetrahydroxy borate anion, which forms 1:2 anionic ester with BEPD, in the alkaline media. And it also clarified that boron extraction was intensive at high BEPD concentrations but stripping at low BEPD and high boron concentrations.

Effect of pH on Boron Stripping

In order to examine the effect of pH on boron stripping, experiments were conducted in a wide pH range of 3-14 at various concentrations of BEPD in the organic phase. The initial concentration of boron in the organic phase was fixed at 0.3 kmol/m$^3$. As shown in Fig. 3, the distribution ratio of boron was constant in the pH range of 3-8 at all BEPD concentrations but the values of it increased with the initial
concentration of BEPD in the organic phase indicating that boron extraction was effective at high BEPD concentrations, especially at BEPD concentration of 3 kmol/m³ the extent of boron extractability was as high as 90 %. In pH range of above 8 to 11 the distribution ratio of boron decreased significantly indicating that boron stripping became predominant with pH. And then the distribution ratio of boron settled down to the same values in the pH range of 11-14 at BEPD concentrations of 0.3 and 1 kmol/m³, and the values of it were very small indicating that over 95 % of boron was stripped from the organic phase so that it was considered that only boron stripping took place in this pH range. From this result, it clarified that the pH dependence of boron distribution ratio on boron extraction and stripping showed the same tendency with that of it on boric acid and tetrahydroxyborate anion, respectively. In addition, it also clarified that BEPD preferred boric acid to tetrahydroxyborate anion to extract so that boron extraction was intensive in acidic media but in alkaline media boron stripping. At BEPD concentration of 3 kmol/m³, however, the distribution ratio of boron stayed at high values at this pH range, furthermore it increased at pH 14 indicating that boron extraction took place in this pH range as discussed in prior paragraph and the extent of boron extractability was 50 % at pH 14. As the reason of the high extractability of boron at pH 14 the high concentration of K⁺ ion as much as 0.55 kmol/m³ was considered since a lot of highly

Fig. 2 The relation between the distribution ratio of boron and the initial concentration of BEPD in the organic phase at various initial concentrations of boron in the aqueous or organic phases. Bₐ or o, i [kmol/m³]: circle, 0.1; triangle, 0.2; square, 0.3; inverse triangle, 0.35; and rhombus, 0.5. Open symbols represent extraction, and closed symbols stripping. The initial pH values of aqueous and stripping phases were 5-6 and over 14, respectively.
concentrated KOH solution was added to adjust the equilibrium pH. From the fact of this, it was regarded that it was interesting to estimate the effect of K+ ion in the stripping phase on boron stripping.

**Effect of K+ Ion Concentration on Boron Stripping**

Boron stripping conducted at various concentrations of K+ ion in the stripping phase. The experimental result is shown in Fig.4. The distribution ratio of boron was the same at low K+ ion concentrations as 0.04-0.075 kmol/m³ representing K+ ions added to adjust the equilibrium pH to 11-13, but it increased significantly with K+ ion concentration at it of above 0.28 kmol/m³ representing K+ ions added to adjust the equilibrium pH to 13.5. This increase indicated that boron extraction became intensive more and more with more K+ ions in the stripping phase but stripping was prevented by it. And consequently the extent of boron extractability reached to over 70 % at K+ ion concentrations of 3 and 4 kmol/m³. From this result, it was considered that boron extraction resulted from the salting out effect of K+ ion added to the counter ion effect so that it was possible to extract boron with BEPD even in the alkaline solution if there were sufficient cations such as Mg²⁺, Ca²⁺, Na⁺ and K⁺ to act as the salting out agents (Pilioenko 1990).

![Fig. 3](image-url)
CONCLUSION

Boron extraction was affected by BEPD concentrations only but stripping by both of boron and BEPD concentrations and boron extraction was intensive at high BEPD concentrations but stripping at high boron concentrations and low BEPD concentrations. From the data of pH dependence of boron distribution ratio it clarified that boron extraction was effective in acidic solutions but stripping in alkaline solutions and BEPD preferred boric acid to tetrahydroxyborate anion to extract. By adding sufficient K\(^+\) ion it was possible to extract boron with BEPD from alkaline solutions but stripping was prevented by it.

ACKNOWLEDGMENT

The authors are grateful to Ms. Yuka Kawano and Ms. Megumi Iikura for their experimental assistance.

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