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Equilibrium of Boron Extraction with 2-Butyl-2-ethyl-1,3-propanediol and 2-Ethylhexanol in Butyl Acetate

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Abstract: Boron extraction with 2-butyl-2-ethyl-1,3-propanediol (BEPD) and 2-ethylhexanol (EHA) in butyl acetate (BA) was carried out at various boron and extractants concentrations. The distribution ratio of boron was constant for all boron concentrations when EHA was used as the extractant, and it increased with EHA concentration. When high concentrations of BEPD were used as the extractant, the distribution ratio of boron was almost the same for all boron concentrations. The distribution ratio of boron increased with BEPD concentrations. An increase in the initial concentration of boron in the aqueous phase severely decreased the boron distribution ratio at low initial concentrations of BEPD in the organic phase. This was caused by the dissolution of BEPD into aqueous solution. The loss of BEPD into the aqueous phase became severe as the concentration of boron in the aqueous phase increased. The loss of EHA was insignificant for all boron concentrations. The distribution ratio of boron was plotted with a function of the equilibrium concentrations of the extractants. The plots showed a linear relation indicating that boron extraction resulted from the same mechanism in all the extraction systems examined in our study. Distribution equations for all the extraction systems were determined.

Keywords: Solvent extraction, boric acid, borate, distribution, extraction mechanism

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INTRODUCTION

Removal of boron from wastewater by solvent extraction has been studied for decades (1–32). Hydroxy compounds, especially 1,3-diols, are most widely used for this purpose. In our previous works, we also studied boron removal from wastewaters using 1,3-diols (2–6). Boron removal and recovery from hot spring water with 2-ethyl-1,3-hexanediol (EHD), which had been considered as the best extractant for boron extraction, dissolved in kerosene, was investigated by Hano et al. (2). The extent of extraction reached was 90% at a pH range of 1–8, but it decreased at a pH above 8. A continuous extraction was performed successfully by using a mixer-settler. However, because of the high solubility of EHD into the aqueous solution, it was considered that EHD is unsuitable for practical use to remove boron from water. Matsumoto et al. examined boron recovery with 2-butyl-2-ethyl-1,3-propanediol (BEPD) and EHD dissolved in various diluents (3). The solubility of BEPD into the aqueous solution was much lower than that of EHD. The distribution ratio of BEPD between organic and aqueous phases was less than 0.001 when 2-ethylhexanol (EHA) was used as the diluent. Continuous recovery of boron from the wastewater of a coal-burning power plant was performed by using BEPD as the extractant and EHA as the diluent by Hirata et al. (5). Boron extracted in the organic phase could be stripped completely by an aqueous alkaline solution of KOH. An equilibrium study of boron extraction with BEPD dissolved in EHA was conducted by Kwon et al. (6). By this particular extraction system using boron extracting alcohols as the extractant and the diluent, an unusual result was obtained. It was considered that boron extraction with BEPD in EHA resulted from a physical action on the basis of boron distribution ratio dependence on boron concentration. It also clarified that boron extraction was under the control of EHA, the diluent, at low BEPD concentrations. In order to estimate the effect of EHA on boron extraction with BEPD dissolved in it, it is necessary to verify the extraction behavior of boron with each BEPD and EHA. In this study, boron extraction equilibrium with BEPD and EHA dissolved in butyl acetate (BA), which is an inert diluent for boron extraction, was investigated at various boron and extractants concentrations. The equilibrium concentrations of the extractants used in our study were measured and then they were plotted against the distribution ratio of boron to clarify the extraction mechanism of boron.

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.

Experimental Procedure

Aqueous solutions were prepared by dissolving boric acid in deionized water for boron concentrations of 0.05–0.3 kmol/m^3. Organic solutions were prepared by dissolving BEPD and EHA in BA for BEPD and EHA concentrations of 0.03–3 kmol/m^3 and 1–6.4 kmol/m^3, respectively. The organic solution of EHA concentration of 6.4 kmol/m^3 is pure EHA. Then equal volumes of aqueous and organic solutions were put into an Erlenmeyer flask, and this was shaken for over 15 h in a thermostated water bath at 25°C. The pH was not adjusted at all for the experiments since the pH of the aqueous boric acid solution was 5–6.

Analyses

After extraction equilibrium was achieved, the mixed solution was allowed to separate into organic and aqueous phases. The concentration of boron in both the aqueous and organic phases was then measured spectrophotometrically by the modified Azomethine H method. The Azomethine H method was modified a little so that the concentration of boron in the organic phase could be also measured. The concentrations of BEPD and EHA in the organic phases were measured by GC-MS (Shimadzu GC-17A) to estimate the loss of the extractants into the aqueous solutions.

RESULTS AND DISCUSSION

Boron Extraction with 2-Ethylhexanol in Butyl Acetate

In order to clarify the effect of EHA on boron extraction with BEPD dissolved in it, boron extraction with EHA dissolved in BA was carried out at various initial concentrations of boron and EHA. The experimental result is shown in Fig. 1. The distribution ratio of boron was constant for all concentrations of boron in the aqueous phase at any initial concentrations of EHA in the organic phase, and it increased with the initial concentrations of EHA. The solid lines in Fig. 1 represent the average values of the boron distribution ratios at each EHA concentration. The experimental result, shown in Fig. 1, verified that boron extraction with EHA resulted from the dissolution of boric acid into the organic phase by a physical action which is a hydrogen bond forming between boric acid and EHA. The values of the boron distribution ratio were so small that the maximum extent of extraction was around 25% when pure EHA was used as the organic solvent. The result being, the variation in the values of the boron distribution ratio at a low EHA concentration of 1 kmol/m^3 was not considered significant. It was considered as an experimental error.

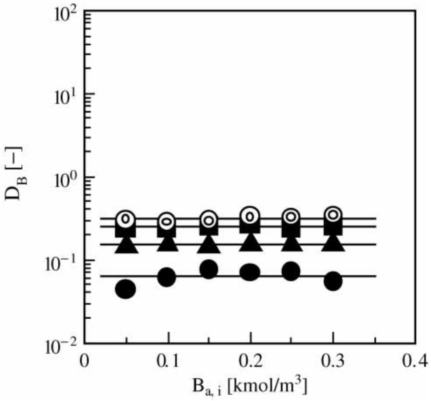

Figure 1. Relation between the initial concentration of boron in the aqueous phase and the distribution ratio of boron at various initial concentration of EHA in the organic phase. $EHA_{o,i}$ [kmol/m^3]: 1, circle; 3, triangle; 5, square; and EHA only, double circle.

Boron Extraction with 2-Butyl-2-Ethyl-1,3-PropaneDiol in Butyl Acetate

Boron extraction with BEPD dissolved in BA was carried out to compare the extraction mechanism with BEPD in BA system with that with BEPD in EHA system which was discussed in our previous work (6). The experimental result is shown in Fig. 2. The distribution ratio of boron was almost the same at any initial concentrations of boron in the aqueous phase when the initial concentrations of BEPD in the organic phase were high, 1 and 3 kmol/m^3. It

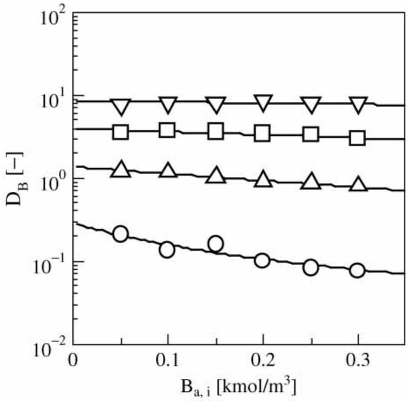

Figure 2. Relation between the initial concentration of boron in the aqueous phase and the distribution ratio of boron at various initial concentrations of BEPD in the organic phase. $BEPD_{o,i}$ [kmol/m^3]: 0.03, circle; 0.3, triangle; 1, square; and 3, inverse triangle.

increased with BEPD concentration. But the distribution ratio of boron decreased significantly with boron concentration at a low BEPD concentration of 0.03 kmol/m^3. The experimental results were well consistent with the solid lines. They were calculated theoretically based on an assumption that boric acid reacts with BEPD to form 1:1 ester in the organic phase. Therefore, it was considered that boric acid in the aqueous phase was extracted into the organic phase by a chemical reaction with BEPD. However, it was also possible that the decrease in the boron distribution ratio was due to the dissolution of BEPD into the aqueous solution since the decrease in the boron distribution ratio was more severe at high boron concentrations and its effect disappeared with an increase in BEPD concentrations. In order to clarify the cause of a decrease in the boron distribution ratio, the equilibrium concentrations of the extractants used in our study were measured after experiments.

The Loss of the Extractants into the Aqueous Phases

The equilibrium concentrations of the extractants were measured by GC-MS to estimate the loss of the extractants into the aqueous phases. The result is partly summarized in Table 1. The loss of BEPD into the aqueous phases became severe with an increase in the initial concentration of boron in the aqueous phase, and the effect of BEPD loss on boron extraction was stronger at low BEPD concentrations. In addition, the loss of BEPD was more significant when BA was used as the diluent than when EHA was used, as expected. In our previous work (3), the loss of BEPD into the aqueous phase was lowered to less than 0.1% by the use of EHA as the diluent of BEPD, the extractant, and EHA was selected as the best diluent for BEPD from the result. In this study, however, the loss of BEPD into the aqueous phase was 5.2–9.5% at the same conditions as 1 kmol/m^3 BEPD in EHA and 1:1 organic phase to aqueous phase volume ratio because an aqueous boric acid solution of 0.1–0.3 kmol/m^3 was used as an aqueous phase instead of deionized water (boric

Table 1. Loss of the extractants into the aqueous phases in percentage [%]

Extraction system	Initial extractant conc. [kmol/m^3]	Initial boron conc. [kmol/m^3] 0.1	0.2	0.3
BEPD/EHA	1.0	5.2	8.9	9.5
	3.0	2.0	5.0	9.0
BEPD/BA	1.0	5.8	10	15
	3.0	1.3	9.3	20
EHA/BA	1.0	1.4	2.2	0.0
	3.0	2.3	0.0	0.0
EHA only	6.4	1.6	1.6	1.6

acid free). The distribution ratio of BEPD between the organic and aqueous phases decreased with an increase in the equilibrium concentration of boron in the aqueous phases (the data is not shown here). Ester formation between boric acid and BEPD in the aqueous phase was considered as the cause of BEPD loss into the aqueous phase (23). On the other hand, the loss of EHA into the aqueous phase was insignificant, (0.0–2.3%), at any initial concentrations of boron (0.1–0.3 kmol/m^3) in the aqueous phase and of EHA (1.0–6.4 (pure EHA) kmol/m^3) in the organic phase. The loss of EHA showed no relations with the equilibrium concentrations of boron in the aqueous phases or with that of EHA in the organic phases. From these results, it was concluded that the loss of BEPD into the aqueous phase resulted from the high affinity between BEPD and boric acid as shown in the extents of boron extraction with BEPD and EHA.

The Equilibrium Concentrations of the Extractants and the Distribution Ratio of Boron

The experimental data on boron extraction with BEPD and EHA were rearranged against the equilibrium concentrations of the extractants since the loss of the extractants was more severe than expected, and the effect of the loss on boron extraction was predictable. The relation of the equilibrium concentrations of the extractants in the organic phases and the distribution ratio of boron is shown in Fig. 3. In all the extraction systems used in our study, the distribution ratio of boron had a proportional relation with the equilibrium concentrations of the extractants. In the case of using BEPD as the extractant, extraction mechanism of boron was the same regardless of the diluent. However, at a low BEPD concentration of 0.03 kmol/m^3, it was clear from the values of the boron distribution ratio that EHA was the extractant for boron extraction not BEPD. In addition, the slope of the plots for EHA in BA system was parallel with the others indicating that the extraction mechanism of boron was the same in all the extraction systems. Distribution equations for all the extraction systems used in our study were obtained from the slopes of the plots in Fig. 3, and they are summarized in Table 2. The extraction ability of BEPD was about 70 times higher than that of EHA. The use of EHA as a diluent of BEPD was the best choice for cost reduction due to the low cost of EHA. EHA was also the best choice for the simple interpretation of the extraction mechanism since EHA prevented the dissolution of BEPD into the aqueous solution so that BEPD could work better as stated previously. Furthermore, by using EHA in extraction, especially at low BEPD concentrations, the distribution ratio of boron did not decrease as much as it did in BEPD in BA system. Therefore, the extraction mechanism could be explained by a simple equation considering physical action (6) even though boron extraction with BEPD might result from a chemical reaction.

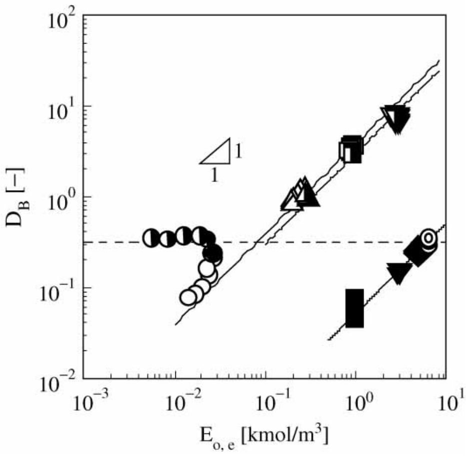

Figure 3. Relation between the equilibrium concentrations of the extractants in the organic phases and the distribution ratio of boron at various initial concentrations of boron in the aqueous phase. $E_{o,\ i}$ [kmol/m^3]: 0.03, circle; 0.3, triangle; 1, square; 3, inverse triangle; 5, rhombus; and EHA only, double circle. BEPD in EHA extraction system, semiclosed key; BEPD in BA extraction system, open key; and EHA in BA extraction system, closed key.

CONCLUSION

On the basis of the boron distribution ratio, it was considered that boron extraction with EHA dissolved in BA resulted from hydrogen bonding but with BEPD dissolved in BA from ester formation. However, it was also possible that boron extraction with the three extraction systems examined in our study took place by the same mechanism, a physical action, from the boron distribution ratio dependence on the equilibrium concentrations of the extractants. The distribution ratio of BEPD decreased with an increase in

Table 2. Distribution equations for the extraction systems used in our study

BEPD in 2-ethylhexanol	$D_B = 2.98\ C_{BEPD} + 0.318$
BEPD in butyl acetate	$D_B = 3.84\ C_{BEPD}$
2-Ethylhexanol in butyl acetate	$D_B = 0.0512\ C_{EHA}$
2-Ethylhexanol only	$D_B = 0.318$

D_B = Distribution ratio of boron [−].
C = Concentration of the extractant [kmol/m^3].

the equilibrium concentration of boron in the aqueous phase because of a high affinity of BEPD to boric acid. The extraction ability of 2-butyl-2-ethyl-1,3-propanediol (BEPD) was much higher than that of 2-ethylhexanol (EHA). It verified that EHA was the optimum diluent for boron extraction with BEPD.

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