Asian Journal of Chemistry Vol. 18, No. 2 (2006), 1277–1284

Extraction of Boron with Diols in Petroleum Benzine and *n*-Amyl Alcohol

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In the present work, the solvent extraction of boron with 2-ethyl-1,3-hexanediol (EHD), 1,2-dihydroxy-4-oxadodecane (DHD) and 3-(4-*tert*-butylphenoxy)-1,2-propanediol (BFPD) in petroleum benzine and *n*-amyl alcohol was thoroughly studied as a function of equilibrium pH. The $pH_{0.5}$ values for EHD, DHD and BFPD were determined from R %-pH graphs as 8.3, 2.7 and 2.3 in *n*-amyl alcohol, respectively. The extraction efficiencies of these diols were also comparatively investigated. The extraction efficiency in both solvents for each extractant was ranged from 78 to 98%. Stripping of boron was achieved as 96% for EHD with NaOH and 81% for BFPD with H_2SO_4.

Key Words: **Boron, Diols, Extraction, Benzine, *n*-Amyl alcohol.**

INTRODUCTION

Boron is not an abundant element, comprising only about 8 mg L^{-1} of the earth's crust. Boron-containing minerals are concentrated in arid regions such as Turkey and California's Death Valley and can be mined cheaply and converted into commercially important boron compounds including $NaBH_4$, an inexpensive bulk chemical. Boron is an essential element for plants and its deficiency affects plant growth and yield in many parts of the world. Boron is a beneficial micronutrient for animals and humans; however, its essentiality has not been established[1]. The tolerable limit of boron content of water is 2–3 mg L^{-1} for citrus and some other agricultural crops, whereas the recommended guideline value is 0.3 mg L^{-1} for drinking water[2].

A high concentration of boron is present in wastewater from boron mines and desulfurizing equipment in steam power stations using coal. Boron contamination

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is also commonly present in magnesium chloride brines and it interferes with the subsequent production of magnesium metal by electrowining operation[3]. Therefore, the high concentration of boron in wastewater and other situations must be reduced to a low level.

Boron can be removed from water by various alternative methods, most of the techniques are difficult to apply and have some disadvantages. These are adsorption and inorganic adsorbents, ion exchange, solvent extraction, a combination of adsorption and solvent extraction, membrane processes and ultra filtration. Among the separation methods, solvent extraction is still an important process because of its time saving and cost effective nature[4]. There are few reports in literature dealing with solvent extraction of boron. In these studies, generally 1,2-diols[4, 5], 1,3-diols[3, 6–13], some catechols[14, 15], phenol and phenol derivatives[16] have been used for solvent extraction of boron. The chemistry of boron indicates that molecules with 1,2-diols are capable of forming neutral boron esters or tetraalkyl borate type of compounds, even in aqueous solutions.

In the present study, boron extraction efficiency of 2-ethyl-1,3-hexanediol (EHD) possessing 1,3-diol and the synthesized 1,2-dihydroxy-4-oxadodecane (DHD) and 3-(4-*t*-butylphenoxy)-1,2-propanediol (BFPD) possessing 1,2-diol functions were examined. The solvent extraction ability of these diols has been studied in petroleum benzine and *n*-amyl alcohol at different pH values and their stripping solutions as well.,

EXPERIMENTAL

Boron concentrations were determined spectrophotometrically by Shimadzu 1601 UV-Visible spectrophotometer. The equilibrium pH was measured by InoLab WTW precision model pH-meter. A Heildolp MR 3001 magnetic stirrer was used in the boron extraction experiments. 2-Ethyl-1,3-hexanediol (EHD) and azomethine-H sodium salt, petroleum benzine (boiling range 80–100°C), *n*-amyl alcohol were obtained from Merck. All other reagents were of analytical reagent grade. In the preparation of solutions doubly distilled water was used.

A stock solution containing 200 mg L^{-1} boron was obtained by dissolving boric acid in doubly distilled water. Working solutions were freshly prepared from the stock solution.

One gram of azomethine-H sodium salt and 3 g of L(+)ascorbic acid were dissolved and made up to 100 mL with water. A buffer solution pH 5.9 was prepared by citric acid and sodium citrate. Equal volumes of azomethine-H solution and buffer solution pH 5.9 were mixed before the analysis for preparing reagent solution used in the determination of boron. The solution stored in plastic bottle must be kept in a refrigerator.

1,2-Dihydroxy-4-oxadodecane (DHD)[5] and 3-(4-*t*-butylphenoxy)-1,2-propanediol (BFPD)[20] were synthesized in the laboratory.

Synthesis of 1,2-dihydroxy-4-oxadodecane

Octanol (211 g, 1.6 mol), racemic glycidol (30 g, 0.4 mol) and catalyst piperidine hydrochloride (0.6 g, 0.005 mol) were stirred at 140–160°C for 10 h. Crude product was distilled in vacuum to give pure (52 g, 63%) of DHD (b.p. 118–120°C/1 mm Hg; ^{1}H NMR: 0.87 (t, 3H), 1.27 (s, 10H), 1.56 (m, 2H), 3.4–3.95 (m, 7H), 2.95 (bs, 1H), 3.25 (bs, 1H); ^{13}C NMR: 14.3, 22.9, 26.4, 29.6, 29.8, 29.9, 32.1, 64.4, 71.2, 72.1, 72.5; Anal. Calcd. for $C_{11}H_{24}O_3$: C, 64.70; H, 11.76; Found: C, 64.52; H, 11.92%).

Synthesis of 3-(4-*t*-butylphenoxy)-1,2-propanediol

4-*t*-Butylphenol (15 g, 0.1 mole), rasemic glycidol (7.4 g, 0.1 mol) and catalyst piperidine hydrochloride (0.6 g, 0.005 mol) were stirred at 70–80°C for 5 h. Crude product was distilled in vacuum to give pure (20.83 g, 93%) of BFPD (b.p. 170–175°C/1 mm Hg; m.p. 86–88°C; ^{1}H NMR ($CDCl_3$): 1.32 (s, 9H), 2.30 (bs, 2H, —OH), 3.74–3.87 (ddd, 2H), 4.04–4.05 (m, 2H), 4.11–4.16 (m, 1H), 6.86–6.88 (m, 2H), 7.33–7.34 (m, 2H); ^{13}C NMR ($CDCl_3$): 154.4, 141.6, 125.7, 114.2, 71.7, 69.9, 66.7, 40.7, 31.4; Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.64; H, 8.96, Found: C, 69 62; H, 8.92%).

Extraction procedure of Boron with EHD, DHD and BFPD

Equal volumes of organic phase containing 0.5 M extractant and aqueous phase containing 4 mg L^{-1} boron at different pH were placed in a stoppered glass round bottom flask for 15 min in a thermostated water bath by stirring at 800 rpm at 25°C. After the completion of extraction, the phases were separated. Initial pHs of aqueous phases were adjusted using NaOH and HCl solutions before the extraction. Boron concentration in the aqueous phase was determined spectrophotometrically[13, 19] by modified azomethine-H method at 414 nm. All experiments were conducted in duplicate. Since the initial concentration of boron is known, the percentage of boron extracted into the organic phase was calculated according to the following equation:

$$R\% = \frac{[B]_i - [B]_e}{[B]_i} \times 100$$

where R% = per cent extraction; $[B]_i$ = initial concentration of boron in aqueous phase; $[B]_e$ = concentration of boron remaining in aqueous phase at equilibrium.

Stripping procedure

Boron extracted to the organic phase was stripped using H_2SO_4 or NaOH solution depending upon the acidity of aqueous phase in the extraction. All experiments were done in duplicate. The percentage of boron stripped from the aqueous phase was calculated according to the following equation:

$$R_s\% = \frac{[B]_i - [B]_e}{V \times [B]_i} \times 100$$

where $R_s\%$ = Percentage of boron stripping; V_{aq} = Aqueous phase volume for stripping; V_{org} = Organic phase volume for stripping; $[B]_{aq}$ = Aqueous phase concentration after stripping (mg L^{-1}); $[B]_{org}$ = Organic phase concentraticn before stripping (mg L^{-1}).

RESULTS AND DISCUSSION

Liquid-liquid extraction of boron from aqueous solution at different equilibrium pH values using EHD, DHD and BFPD as diols in petroleum benzine and *n*-amyl alcohol were studied. Petroleum benzine having low polarity and low price was preferred as a suitable solvent for EHD and DHD. Due to very low solubility of BFPD in petroleum benzine, *n*-amyl alcohol was chosen. Also, these solvents were chosen depending on the high degree extractant efficiencies of the studied diols.

Firstly, the effect of different concentrations of EHD in petroleum benzine and *n*-amyl alcohol for boron extraction from aqueous solution was investigated at different equilibrium pH values. The extraction efficiency of boron with EHD depending on pHs in petroleum benzene was shown in Fig. 1. The per cent recovery of boron was high and stable above 0.5 M of EHD in petroleum benzine.

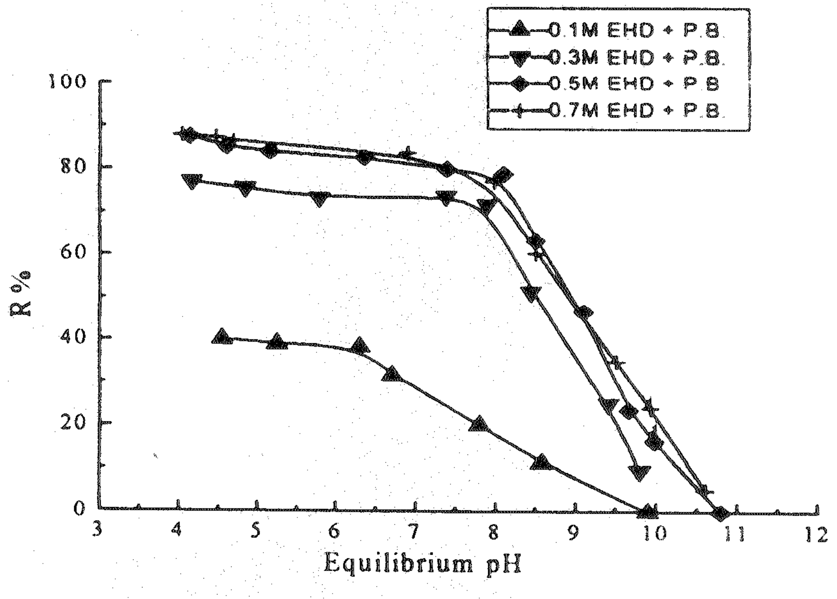

Fig. 1. pH dependence of boron extraction at different [EHD] in petroleum benzine. [B] = 4 mg L^{-1}

In *n*-amyl alcohol (Fig. 2), the extraction efficiency of boron was given only for 0.5 M EHD at different pHs because of its low extractability at lower extractant concentration as observed in petroleum benzine. The high extractable pH at this EHD concentration was in the range of 4.2–8.0 and 3.4–8.0 in petroleum benzine and *n*-amyl alcohol. The optimum organic phase concentration as 0.5 M at pH 4.2 and pH 3.4 in petroleum benzine and *n*-amyl alcohol, respectively were chosen as the best extraction yield for EHD. Boron extraction yield is 88% in petroleum benzine and 74% in *n*-amyl alcohol with EHD. The percentage recovery of boron in EHD in petroleum benzene is higher, 14% more, than in *n*-amyl alcohol.

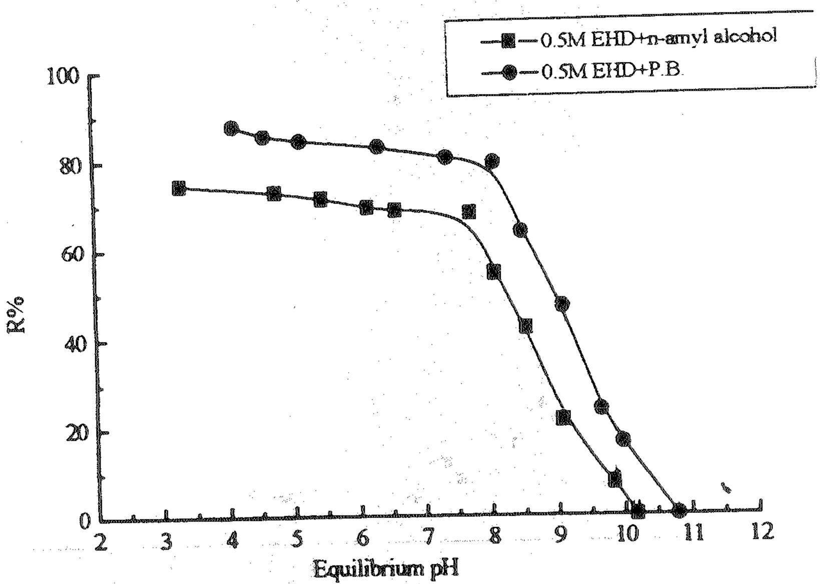

Fig. 2. The influence of solvents and pH values on R% using 0.5 M EHD

The extraction efficiency of boron with DHD in petroleum benzine and *n*-amyl alcohol was shown in Fig. 3. The highest extraction value with 0.5 M DHD was 80 and 78% at pH 2.1 in petroleum benzine and *n*-amyl alcohol, respectively. It can be concluded that the recovery ratio of boron with DHD in both solvents was very close to 1.

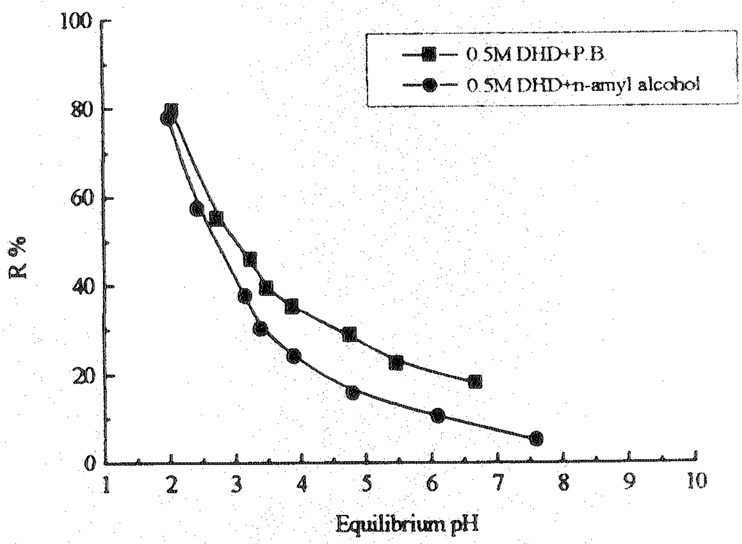

Fig. 3. The influence of solvents and pH values on R% using 0.5 M DHD

The extraction ability of BFPD diol was investigated as a function of its concentration at different equilibrium pH values in *n*-amyl alcohol due to undissolving in petroleum benzine (Fig. 4). The highest extraction values were recorded 97% at pH 1.1 for 0.5 M and 98% at pH 1.2 for 0.7 M of BFPD. The most satisfactory extraction results were obtained with BFPD in *n*-amyl alcohol at strongly acidic range of aqueous solutions.

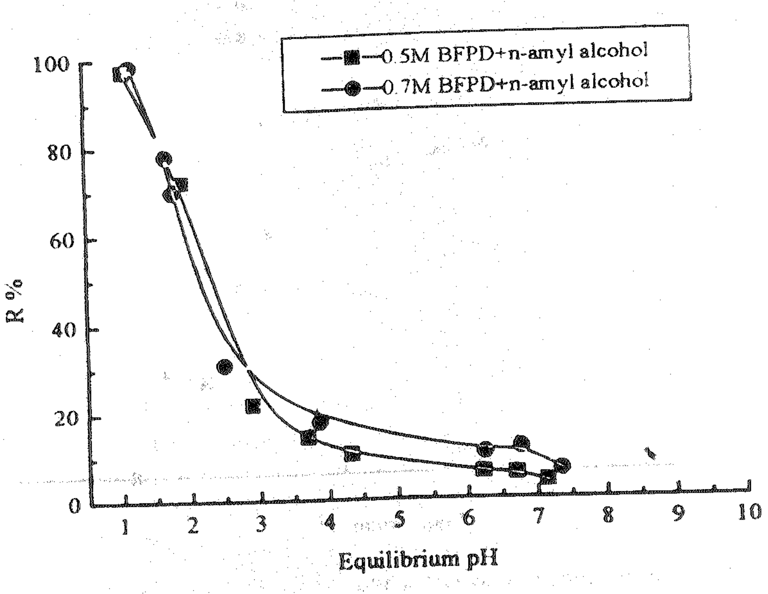

Fig. 4. The influence of [BFPD] on R% at different equilibrium pH values, [B] = 4 mg L^{-1}

The extraction efficiencies of EHD and DHD were high but it can be said that the extraction efficiency of EHD was slightly better than DHD in petroleum benzine. In *n*-amyl alcohol, the increasing order of the boron extraction yield is EHD, DHD, BFPD, respectively.

On the other hand, the $pH_{0.5}$ values for the extraction efficiencies of EHD, DHD and BFPD were also determined using R%-pH graphs (Table-1). Results showed that the $pH_{0.5}$ values for EHD in both solvents were in basic medium. However, the $pH_{0.5}$ values for DHD and BFPD in studied solvents were in acidic medium. It can be stated that anionic borate ester formation seems to be less favourable in the case of vicinal diols. pH-Dependent boron loading experiments indicate that the neutral boron esters in the solution is stable at strong pH values. The results of this study are consistent with those observed in iminodipropylene glycol functions[21].

TABLE-1
$pH_{0.5}$ VALUES OF EHD, BFPD, DHD

Solvent	0.5 M EHD	0.5 M DHD	0.5 M BFPD
Petroleum benzine	8.9	3.1	—
n-Amyl alcohol	8.3	2.7	2.3

Stripping of boron is a very important criterion for boron extraction systems; so boron was back extracted from EHD in petroleum benzine using H_2SO_4 and NaOH solutions as presented in Table-2.

TABLE-2
STRIPPING OF BORON FROM 0.5 M EHD IN PETROLEUM BENZINE AND *n*-AMYL ALCOHOL

Petroleum benzine			*N*-Amyl alcohol		
Stripping equilibrium pH	C_{eq}/ppm	R_s %	Stripping equilibrium pH	C_{eq}/ppm	R_s %
1.7	0.54	32	2.4	0.28	20
2.7	0.60	36	2.8	0.53	39
5.8	0.72	43	3.0	0.60	42
8.7	1.28	76	3.8	1.50	76
9.2	1.56	93	4.1	1.58	81
10.5	1.60	96			

In all stripping studies, the samples in which extraction yields were 84% were used. As stripping solutions, 1×10^{-2} to 1×10^{-3} mol L^{-1} H_2SO_4, distilled water and 1×10^{-3} mol L^{-1} NaOH solutions were tested. As a result, 96% of boron from EHD in petroleum benzine was recovered using 1×10^{-3} mol L^{-1} NaOH solution. On the other hand, H_2SO_4 solutions were only used in boron stripping from BFPD in *n*-amyl alcohol. In all stripping studies, the samples in which extraction yields were 98% were used. As stripping solutions, 1×10^{-2} to 1×10^{-4} M H_2SO_4 solutions were tested. After stripping, 81% of boron from BFPD in *n*-amyl alcohol was recovered by using 2×10^{-4} M H_2SO_4 solutions. High recovery percentage in stripping studies with EHD was accomplished in basic medium, whereas with BFPD, in slightly strong acidic medium. The pH change is also an important factor for BFPD to get high stripping recovery. The stripping recovery with DHD was only increased up to 40% in whether basic or moderate acidic medium.

In conclusion, the DHD and BFPD which have *vic*-diol functions and EHD which has 1,3-diol functions exhibit reasonable efficiency at low $pH_{0.5}$ values and high $pH_{0.5}$ values, respectively in both solvents in extraction of boron from aqueous solutions. Since BFPD is readily obtainable from simple reagents, it can be considered alternatively as a potential candidate extractant in large-scale boron removal.

ACKNOWLEDGEMENTS

The authors are grateful to Research Foundation of Dokuz Eylül University (Project 04-KB-FEN-022) for the financial support.

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(*Received*: 21 June 2005; *Accepted:* 22 December 2005) AJC-4564