Investigation of Some 1,3-Diols for the Requirements of Solvent Extraction of Boron: 2,2,6-Trimethyl-1,3 Heptanediol as a Potential Boron Extractant

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Eighteen 1,3-diols were synthesized and their structure and distribution ratio for the solvent extraction of boron were studied. Diols with a high distribution ratio ($D_{B(OH)_3} > 10$) were investigated for the requirements of solvent extraction of boron. Their extraction capacity, and solubility in aqueous phase and in organic diluents were investigated by comparison to 2-ethyl-1,3-hexanediol (EHD), which is widely used as a boron extractant. Among a series of 1,3 diols, 1-benzyl-2,2-dimethyl-1,3-propanediol (4a) and 2,2,6-trimethyl-1,3-heptanediol (3a) were found to have very low solubility in the aqueous phase compared to the others. IPD (3a) was found to have a high solubility in aliphatic diluents such as kerosene. IPD, which has good solubility properties for the solvent extraction of boron, was studied in detail, including dependence of pH, diol concentration, and stripping facility, and in various organic diluents.

Introduction

Even though boron is an important micronutrient for plants, animals, and humans, the range between its deficiency and excess is narrow.[1] The tolerable limit of the boron content of water is 2 or 3 ppm for citrus and some other agricultural crops,[2] whereas the recommended guideline is 0.3 ppm for drinking water.[3] Currently, the removal of boron from water remains a challenging problem. Since the world's largest boron sources are located in Turkey, boron pollution presents a severe problem for the country. For instance, large areas around the Menderes River in west Anatolia suffered from boron pollution caused by geothermal sources and boron mines.[4,5]

The concentration of boron in wastewater and other situations must be reduced to low levels. Among the separation techniques, solvent extraction is still an important process because of its time saving and cost effective nature, and the potential to remove a large amount of boron at one time.[6] Removal of boron from wastewater by solvent extraction has been studied for decades.[1−13] Hydroxy compounds, especially 1,3-diols, are most commonly used for this purpose.

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The extraction ability and distribution value of various 1,3-diols have been studied by Egneus and Uppström[7,8], but not in detail. On the other hand, 18 new 1,3-diols with methyl and geminal methyl groups at the second carbon and with various side chains (benzyl, isoalkyl, and n-alkyl groups) at the third carbon have been designed and synthesized our group[9,10] In our previous studies they were considered for their extracting ability, but their solubility in aqueous phase and the ability of extraction at low concentration in organic phase were not examined in the solvent extraction of boron.

Boron removal and recovery from hot spring water with EHD dissolved in kerosene, which was considered the best extractant for boron, was investigated by Hano et al.;[11] however, because of the high solubility of EHD into the aqueous phase, it was considered unsuitable for removing boron from water.

BEPD (2-butyl-2-ethyl-1, 3-propanediol)[12] and IBD (2,2,5 trimethyl-1,3 hexanediol)[10] have been used for recovery of boric acid in extraction systems with reasonable efficiency due to the fact that they are more lipophilic extractants than EHD.

In the present study, among the series of eighteen 1,3 diols, 8, which are the best according to their high boron distribution coefficients ($D_{B(OH)3} > 10$), were chosen and we examined their solubility, extraction capacity, and other requirements. Among these, 2,2,6,-trimethyl-1,3-heptanediol, which has good extraction ability and solubility for the solvent extraction of boron, was studied in detail, including dependence on pH, diol concentration, stripping facility, and percentage of recovery in various organic diluents.

Experimental

Apparatus

The equilibrium pH was measured with a Denver Basic pH meter. Boron concentrations in the aqueous phase were determined spectrometrically with a Unicam Uv2 UV-visible spectrophotometer.

The concentrations of 1,3-diols and EHD in the organic phase were measured with a Shimadzu GC-14A Gas chromatograph to estimate the loss of the extractants into the aqueous solutions.

Synthesis of 1,3-diols: 1,3-Diols were synthesized according to previous reports.[9,10]

Reagents and solutions

Standard boron solution: A 0.01 M boron stock solution was prepared by dissolving boric acid in aqueous solution at I = 0.5 M. Working solutions were prepared by accurate dilutions of the stock solution.

Azomethine-H solution: One gram of azomethine-H sodium salt ($C_{17}H_{12}NNaO_8S_2$) and 3 g of L(+)-ascorbic acid ($C_6H_8O_6$) were dissolved and brought to 100 mL with deionized water. The solution was stored in a plastic bottle and remained stable for approximately 1 week while stored in a refrigerator at 4 °C.

Buffer solution (pH 5.9): Citric acid (28.88 mL, 0.002 M) and sodium citrate (19.41 mL, 0.001 M) were mixed and brought to 100 mL with deionized water.

Reagent solution: Equal volumes of azomethine–H solution and buffer solution (pH 5.9) were mixed before the analysis. The solution was kept in a refrigerator.

All reagents were purchased from Fluka or Merck and were used without further purification.

Distribution experiments

The extraction experiments were carried out in a specially designed jacketed glass tube. The jacket was connected to a thermostated water supply (25 ± 0.1 °C). The parameters used throughout the experiment were as follows: organic (O):aqueous (A) phase ratio of 1:1; temperature: 25 °C; contact time: 15 min; stirring rate: 1300 rpm. After the extraction was completed, the phases were separated by gravity for 30 min; the equilibrium pH of the aqueous phase was then measured. Boron concentrations in the aqueous phase at certain equilibrium values were determined spectrophotometrically by the azomethine-H method.[14] The following procedure was used for each sample: 4-10 standards and samples were treated simultaneously. An aliquot of standard boron solution containing up to 0.3 ppm was placed in a 10-mL test tube equipped with a stopper. Then, 2 mL of reagent solution was added to each of the solutions and the absorbance was measured at 414 nm using a 10-mm quartz cell, with a reagent solution as a reference. The azomethine-H method[13,14] was modified since the determination of boron was performed at various pH values in the aqueous phase.

Before the preparation of the 1,3-diol solutions, chloroform was washed with redistilled water, and then the boron solution, with an ionic strength (I) of 0.5 M, was prepared with 0.49 M sodium chloride and 0.01 M hydrochloric acid. Distribution experiments were carried out at pH 2 with 0.01 M boron solution.

Results and Discussion

Among various substance classes, it is known that 1,3-diols have maximum extraction capacity for the solvent extraction of boron.[9] Previously 1°,2° or 1°,3° classes of 1,3-diols, which have a methyl and 2 geminal methyls at the second carbon and benzyl, isopropyl, isobutyl, and isopentyl groups as a side chain at the third carbon, were found to be the best structures according to the boron distribution coefficient ($D_{B(OH)3} > 10$), but have not been examined for the other requirements, such as solubility in the aqueous phase and in organic diluent, extraction capacity, volatility, stripping facility, etc.[9,10] The relationship between the recovery values of extracted boron from the aqueous phase and various concentrations of diols in chloroform are shown in Table 1. The maximum extraction capacity was reached at 0.4 M concentration in chloroform for all diols, with other factors being constant (equilibrium pH: 2; I: 0.5; initial boron concentration: 0.01 M). As can be seen from Table 1, all of the tested diols have high extraction capacity, but the extractants 4a, 3a, and 3b are just slightly more effective. In our previous studies[9,10] and in other works, it has been found that as the hydrophobic character of diols increases their extraction capacity decreases in more polar solvents, such as CHCl$_3$, and vice versa.

The relationship between the recovery values of extracted boron from the aqueous phase and various concentrations of IPD and EHD was also studied in kerosene. As shown in Table 1, the maximum extraction capacity was reached at 0.3 M EHD (69.8%) and 0.1 M IPD (93.3%) diol concentration in kerosene.

The loss of extractant, recovery of boron, distribution coefficient, and other physical properties are shown in Table 2. All of them, except 2b, which has a high b.p., are solid. All diols are non-volatile and non-flammable. They are not reported elsewhere as toxic materials. As it can be seen in Table 2, all tested diols have a high distribution coefficient ($D_{B(OH)3} > 10$) and high boron recovery. The extractant 1a, 1b, and EHD have a high distribution coefficient and extraction ability, but high solubility in the aqueous phase and insufficient solubility in aliphatic hydrocarbon diluents; therefore, they were found to be unsuitable extractants for the solvent extraction of boron.

Table 1. The relationship between the concentration of diols and EHD in chloroform, and in kerosene, and recovery values of boron ($\pm$ 2). Boron: 0.01 M; initial pH: 6; equilibrium pH: 2; I = 0.5.

Concentration of diols (M)	Recovery of boron in chloroform (%)									Recovery of boron in kerosene (%)	
	1a	1b	2a	2b	3a	3b	4a	4b	EHD	3a	EHD
0.025	28.2	32.4	26.3	31.0	24.2	35.3	4.6	19.8	30.4	25.3	3.5
0.05	55.3	62.4	45.3	47.3	37.5	44.6	19.9	33.1	52.9	70.9	10.3
0.075	65.9	70.5	53.5	59.5	67.0	62.7	50.2	69.4	67.8	82.0	19.9
0.1	88.3	89.5	74.0	79.0	71.7	66.3	60.1	75.1	76.3	85.4	29.4
0.2	90.3	91.4	80.8	90.0	79.8	80.1	78.1	86.1	84.3	91.2	55.7
0.3	91.8	94.1	90.0	93.0	81.7	87.6	88.3	94.4	90.8	93.3	69.8
0.4	94.2	95.3	93.0	95.1	91.2	91.7	90.3	94.9	94.1	94.7	73.6
0.5	96.0	97.0	95.0	96.0	91.4	94.1	92.1	95.2	96.2	95.1	78.8

In the solvent extraction process, most of the cost is attributed to the loss of extractant. On the other hand, the carrier solvents should be inexpensive, non-toxic, and non-flammable. Therefore, kerosene and IPD were selected as the carrier and extractant for the solvent extraction of boron, respectively. Because of the high water solubility problems of EHD[11] and BEPD[12], stripping difficulties of CTMP[13], and their insufficient solubility in inexpensive solvents, IPD was chosen as a potential extractant and was studied in detail and compared to EHD.
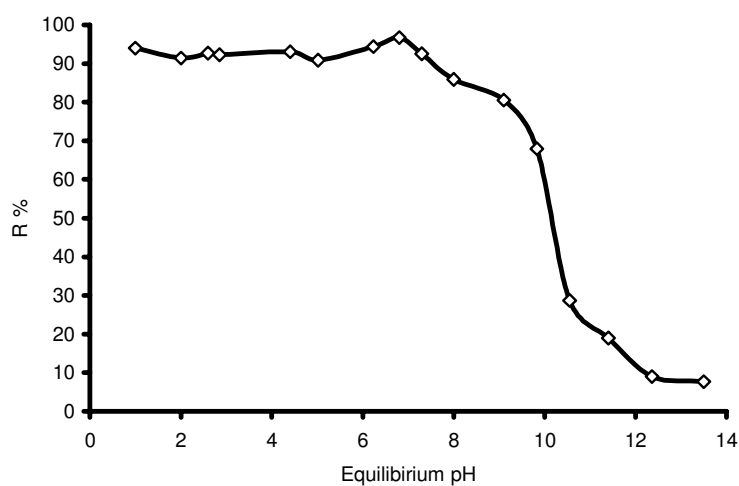

Figure. The effect of pH on the % extraction of boron with IPD (aqueous phase: 0.01 M boron (I = 0.5 M); organic phase: 0.5 M IPD in chloroform).

Table 2. The comparison of boron extractants.

Extractant Name	[a]The Loss of extractant (%)	[b]Recovery %	[b]Distribution of $B(OH)_3$	m.p. °C	[c]highly soluble solvent	Classes (hydroxyl group) Substitution (at second carbon) side chain
2,2,4-trimethyl-1,3-pentanediol (1a)	3,0	96.9	31.7	46-47	[e]$CHCl_3$	1°,2° Geminal methyl isopropyl
2,3,4-trimethyl-1,3-pentanediol (1b)	3,2	96.3	25.7	69-70	[e]$CHCl_3$	1°,3° methyl isopropyl
[f]2,2,5-trimethyl-1,3-hexanediol (2a)	0.55	96.8	30.3	79-81	[e]$CHCl_3$	1°,2° Geminal methyl isobutyl
2,3,5-trimethyl-1,3-hexanediol (2b)	0.77	96.2	25.6	[d] 83-84 (0.5)	kerosene	1°,3° methyl isobutyl
[g]2,2,6-trimethyl-1,3-heptanediol (3a)	0.33	91.4 [g]95.1	10.7 [g]19.4	41-42	kerosene	1°,2° Geminal methyl isopentyl
2,3,6-trimethyl-1,3-heptanediol (3b)	0.45	94.8	18.2	28-29	kerosene	1°,3° methyl isopentyl
1-benzy-2,2-dimethyl-1,3-propanediol (4a)	0.22	63.9	14.7	85-86	toluene	1°,2° Geminal methyl benzyl
1-benzyl -1-methyl- 1,3-propanediol (4b)	0.66	75.5	20.5	66-67	toluene	1°,3° methyl benzyl
2-ethyl-1,3-hexanediol (EHD)	4,18	96.2 [g]78.8	25.3 [g]3.7	[d]243-244	[e]$CHCl_3$	1°,2° ethyl butyl

[a] The concentrations of extractants in the organic phases were measured by GC.

[b] Recovery % and distribution data for 0.01 M boric acid in aqueous solution by 0.5 M diols in chloroform at the equilibrium pH of 2 and at constant ionic strength (I = 0.5).[9,10]

[c] Extractant, which has a good solubility in kerosene (up to 0.5 M).

[d] B.p. (mmHg).

[e] They are not sufficiently soluble in aliphatic diluents. They are only soluble in chloroform.

[f] The best stripping values, 96.7%[10] and 98.8%, were obtained with a single stripping stage by using 0.1 M solution of NaOH for 2a and 3a, respectively.

[g] Recovery % and distribution data for 0.01 M boric acid in aqueous solution by 0.5 M diols in kerosene at an equilibrium pH of 2 and at constant ionic strength (I = 0.5).

The effect of pH on the extraction percentage of boron with IPD was studied in chloroform. The highest extraction values were obtained in the pH range of 1-7. The highest recovery value (96.7%) was obtained at pH 6.80, but it decreased above the equilibrium pH values as shown in the Figure. Therefore, it can be concluded that boron extraction with IPD was effective in an acidic medium and ineffective in an alkaline medium (pH < 8.30); but, at pH values > 8, the extent of boron extraction decreases because the boron is released from its complex form. Kerosene, chloroform, n-amyl alcohol, toluene, n-hexane, and petroleum benzene were also examined as carrier solvents with IPD. Among these, kerosene was found to be the best solvent for IPD, as shown in Table 3. This is an advantage for IPD as an extractant for the solvent extraction of boron; this result supports our previous suggestion.

Table 3. The effect of various solvents used as carriers on the extraction of boron with IPD.

Solvent	Kerosene	chloroform	n-hexane	toluene	Petroleum Benzine	n-Amyl Alcohol
Recovery of boron (%)	94.1	91.5	91.3	78.7	78.2	72.7

*Aqeuous phase: 0.01 M boron (5 mL, I = 0.5); organic phase: 0.5 M IPD (5 mL).

After the extraction, the boron-loaded organic phase was treated with an alkaline solution, whereby the boron was stripped from the organic phase into the aqueous alkaline phase. As can be seen from Tables 4 and 5, in all tested NaOH concentrations, the stripping yields in kerosene are higher than those in chloroform in the same (O:A) stripping volume ratio. The best stripping yields (98.8% and 97.0%) were obtained in chloroform and kerosene at the single stage by using 0.1 M NaOH and 0.05 M NaOH solution, respectively.

Table 4. Stripping of loaded IPD in chloroform with different base concentrations.

Stripping base NaOH (M)	Stripping vol. ratio (extractant:base)	Aqueous Phase		Boron in organic phase after stripping (ppm)	Boron in aqueous phase after stripping (ppm)	Stripping yield %
		Init. pH	Equil. pH			
0.1	3:1	12.90	12.52	1.2	310	98.8
0.05	3:1	12.58	11.92	10.2	283	90.2
0.025	3:1	12.05	11.09	38.2	199	63.5
0.01	3:1	11.80	10.45	78.5	78	24.9

*Boron concentration in the organic phase: 104.5 ppm; organic phase: 0.5 M IPD in chloroform (50 mL); aqueous phase: 0.01 M boron (50 mL); equilibrium pH: 6.80; R %: 96.7

In conclusion, IPD has high extraction ability at a wide range of pHs, low solubility in water, high solubility in kerosene, and good stripping facility; therefore, all these properties make it a potentially powerful extractant for the solvent extraction of boron in industrial applications.

Table 5. Stripping of loaded IPD in kerosene with different base concentrations (I = 0.5 M).

Stripping base NaOH (M)	Stripping vol. ratio (extractant:base)	Aqueous Phase		Boron in organic phase after stripping (ppm)	Boron in aqueous phase after stripping (ppm)	Stripping yield (%)
		Init. pH	Equil. pH			
0.05	3:1	12.39	12.05	8.3	269.1	97.0
0.035	3:1	12.11	11.43	32.9	244.5	88.1
0.025	3:1	12.20	10.70	46.1	231.3	83.4
0.02	3:1	12.05	10.42	99.8	177.6	64.0
0.015	3:1	11.98	10.10	138.3	139.1	50.2
0.01	3:1	11.78	9.95	174.1	102.8	37.1
0.05	1:1	12.39	12.40	3.7	88.8	96.0
0.01	1:1	11.77	9.99	11.8	80.6	87.2
0.075	1:1	11.56	9.82	12.0	80.5	86.9
0.005	1:1	11.47	9.51	41.3	51.2	55.4
0.0025	1:1	11.32	9.11	57.3	35.1	38.0
0.001	1:1	10.76	8.02	73.2	19.3	20.9

*Boron concentration in the organic phase: 92.48 ppm; organic phase: 0.1 M IPD in kerosene (50 mL); aqueous phase: 0.01 M boron (50 mL); equilibrium pH: 6; R %: 85.4.

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