

EXTRACTION OF BORON AS ITS COMPLEX WITH 2,3-NAPHTHALENEDIOL

F. VLÁČIL^a and K. DRBAL^b

^a Department of Analytical Chemistry,

Institute of Chemical Technology, 166 28 Prague and

^b Department of Chemistry, Institute of Agriculture, 370 00 České Budějovice

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The extraction of boric acid has been studied using an extractant containing n-butanol, 2,3-naphthalenediol and one of the following three substances yielding a hydrophobic organic cation, diphenylguanidine, n-octadecylamine and tetraphenylarsonium chloride. The dependence of the recovery of the boron extraction in this system on the pH, the reagent concentration, the ionic strength and the temperature were monitored. Under suitable conditions, 96 to 98% of the boron is extracted with a 2,3-naphthalenediol solution in the presence of any of the three above substances. A solution of 2,3-naphthalenediol and diphenylguanidine in n-butanol is recommended for support impregnation in the extraction chromatography of boron.

In a previous communication¹, the selection of a suitable extraction system for the isolation of boron by extraction chromatography was described. Among the numerous reagents and solvents tested, 2,3-naphthalenediol (ND), forming a complex anion with boric acid (under the studied conditions most probably $[B(OH)_2L]^-$, where H_2L is ND), was found to be most suitable; diphenylguanidine (DPG), tetraphenylarsonium chloride (TPA) and n-octadecylamine (ODA) were found to be best substances yielding cation X^+ to form the extractable ion-associate, $\{X^+, [B(OH)_2L]^- \}$, under suitable conditions. Among the solvents tested n-butanol proved best for extraction of this ion-associate.

The purpose of this work was to find the optimum conditions for the static extraction of boron in the above systems, which would enable development of a boron isolation method using extraction chromatography.

EXPERIMENTAL

Chemicals and Instruments

The manufacturers of the chemicals used and the methods for their purification were specified in the previous paper¹, where the pH measurement and the determination of boron in the individual phases after the extraction were also described. The extraction was performed in ground-glass stoppered test tubes on a horizontal shaker; the content of the test-tubes was then centrifuged for rapid phase separation. The aqueous phase was removed using a syringe. Unless otherwise stated, the extractions were carried out at laboratory temperature ($20 \pm 1^\circ C$), with $V_{org} =$

$= V_{\text{aq}}$. It was verified experimentally that extraction equilibrium was always achieved in less than ten minutes. If the effect of the ionic strength on the boron percentage extraction was not monitored, it was maintained constant at $I = 0.1$ (Na_2SO_4) (see ref.¹).

RESULTS

Extraction with n-Butanol in the Presence of Diphenylguanidine

The effect of the pH of the aqueous solution on the percentage boron extraction was monitored in the range from 1.5 to 11.5 under the conditions evident from Fig. 1. The concentration data in this and all the other figures are the initial concentrations of ND, DPG or ODA in the organic phase and of boron in the aqueous phase.

Further, the dependence of the percentage boron extraction on the ND concentration was monitored at pH 2.32, *i.e.*, in the region of maximum boron extraction with both ND concentrations used in the extractant. The results obtained and the other conditions for this dependence are given in Fig. 2. The effect of the DPG concentration on the percentage boron extraction is depicted in Fig. 3 and was studied at pH values of 2.31, 3.51 and 4.09, corresponding to percentage extraction maxima at various DPG concentrations. The DPG concentration was not increased above a value

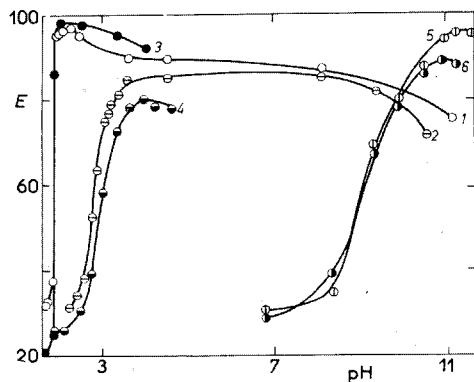


FIG. 1

The pH-Effect on the Percentage Boron Extraction with 2,3-Naphthalenediol and Diphenylguanidine (n-Octadecylamine, Tetraphenylarsonium chloride) in n-Butanol

$c_B = 3.3 \cdot 10^{-3} \text{ M}$, $c_{\text{ND}} = 5.0 \cdot 10^{-2} \text{ M}$, $I = 0.1$, $V_{\text{org}} = V_{\text{aq}}$. c_{DPG} : 1 $5 \cdot 10^{-2} \text{ M}$; 2 $5 \cdot 10^{-3} \text{ M}$; c_{ODA} : 3 $4.25 \cdot 10^{-2} \text{ M}$; 4 $5.25 \cdot 10^{-3} \text{ M}$; c_{TPA} : 5 $5 \cdot 10^{-2} \text{ M}$; 6 $5 \cdot 10^{-3} \text{ M}$.

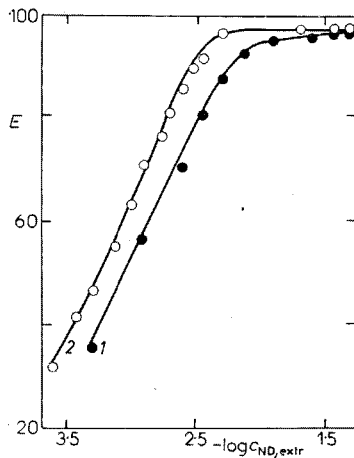


FIG. 2

The Effect of the 2,3-Naphthalenediol Concentration in n-Butanol on the Percentage Boron Extraction in the Presence of Diphenylguanidine

pH 2.32, $c_{\text{DPG}} = 5 \cdot 10^{-2} \text{ M}$, $c_B = 3.3 \cdot 10^{-3} \text{ M}$ (1) and $1.28 \cdot 10^{-3} \text{ M}$ (2) $I = 0.1$, $V_{\text{org}} = V_{\text{aq}}$.

of $5.0 \cdot 10^{-2}M$, as a solid phase separated during the extraction at higher values. The effect of the ionic strength of the aqueous solution, determined at pH 2.2 to 2.3 and constant concentrations of ND ($5.0 \cdot 10^{-2}M$), boron ($3.30 \cdot 10^{-3}M$) and DPG ($5.0 \cdot 10^{-2}M$), is evident from the following table:

| | | | | | |
|---------------|------|------|------|------|------|
| <i>I</i> : | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 |
| <i>E</i> , %: | 96.8 | 98.3 | 98.0 | 97.7 | 97.3 |

Sodium sulphate was used for ionic strength adjustment. The effect of the boron concentration on its percentage extraction was monitored in the range from $6.45 \cdot 10^{-4}$ to $3.07 \cdot 10^{-2}M$ at pH 2.2; the other conditions are given in Fig. 4. The effect of the temperature was studied by shaking the extraction mixture in a water bath at temperature in the range 10–73°C; after phase separation, the aqueous phase was brought to 20°C and an aliquot pipetted for the determination. In this temperature range, the differences in the percentage extraction did not significantly exceed the error of the boron determination.

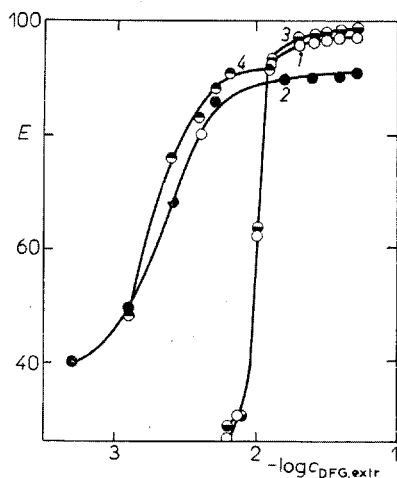


FIG. 3

The Effect of the Diphenylguanidine Concentration on the Percentage Boron Extraction with a 2,3-Naphthalenediol Solution in *n*-Butanol

$c_{ND} = 5.0 \cdot 10^{-2}M$, I 0.1, $V_{org} = V_{aq}$. c_B :
1, $2.33 \cdot 10^{-3}M$; 3, $4.128 \cdot 10^{-3}M$. pH: 1, 3
2.31; 2.409; 4.351.

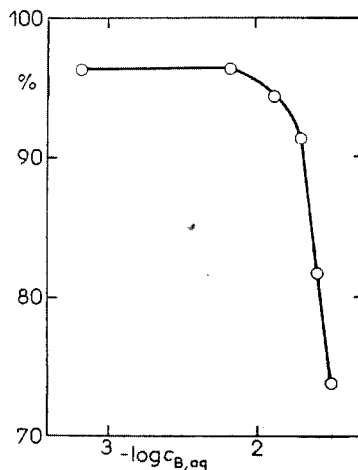


FIG. 4

The Dependence of the Boron Percentage Extraction on its Initial Concentration in the Aqueous Phase

$c_{ND} = c_{DPG} = 5.0 \cdot 10^{-2}M$, I 0.1, pH 2.2,
 $V_{org} = V_{aq}$.

The effect of various anions on the percentage boron extraction was studied under the same conditions as those used for the study of the effect of the ionic strength. The effect of PO_4^{3-} , Cl^- , SiO_3^{2-} and NO_3^- , *i.e.* those anions which can be assumed to be present in plant ashes, was studied in the concentration range, 10–100 mg/l. Only nitrate interferes; it decreases the absorbance of the measured aqueous solutions in the photometric determination of boric acid with quinalizarine.

Extraction with n-Butanol in the Presence of Tetraphenylarsonium Chloride

The effect of the pH and the conditions used are illustrated in Fig. 1. The effect of the ND concentration on the boron extraction in the presence of TPA is given in Fig. 5 and the effect of the TPA concentration (in the form of chloride) on the percentage boron extraction at pH 11.23 in Fig. 6.

Extraction with n-Butanol in the Presence of n-Octadecylamine

Octadecylamine solutions were obtained by adding the required amount of 2M-NaOH to the calculated amount of the chloride and extracting the pulpy mixture with n-butanol. The organic phase obtained was repeatedly washed after separation

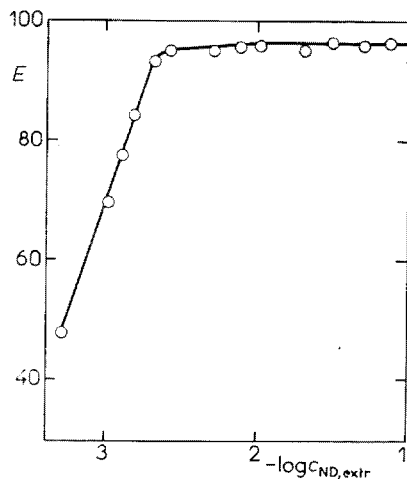


FIG. 5

The Effect of the Concentration of 2,3-Naphthalenediol in n-Butanol on the Percentage Boron Extraction in the Presence of Tetraphenylarsonium Ions

$c_{\text{B}} = 1.7 \cdot 10^{-3} \text{M}$, $c_{\text{TPA}} = 5 \cdot 10^{-2} \text{M}$, pH 11.30, $I 0.1$, $V_{\text{org}} = V_{\text{aq}}$.

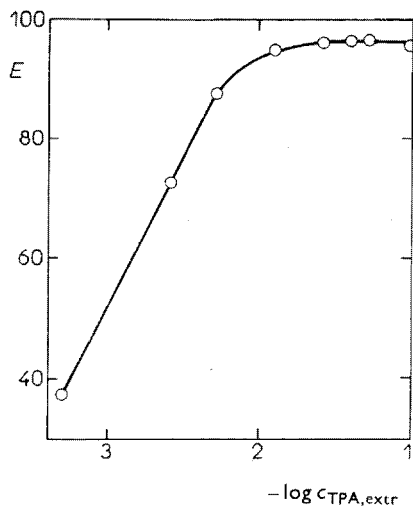


FIG. 6

The Effect of the Concentration of Tetraphenylarsonium Chloride on the Percentage Boron Extraction with 2,3-Naphthalenediol in n-Butanol

$c_{\text{B}} = 3.21 \cdot 10^{-3} \text{M}$, $c_{\text{ND}} = 5 \cdot 10^{-2} \text{M}$, pH 11.23, $I 0.1$, $V_{\text{org}} = V_{\text{aq}}$.

with solvent- and octadecylamine-saturated water, until the aqueous washings were almost neutral. The amine solution obtained was then transferred to a volumetric flask, diluted to the mark and, after mineralization, the octadecylamine concentration was determined photometrically with the Nessler reagent.

The pH-effect (Fig. 1) was monitored in the range from pH 1.68 to 4.62. A precipitate appeared in the aqueous phase at pH < 2, but did not contain a detectable amount of boron.

The effect of the ODA and ND concentrations is given in Figs 7 and 8, together with the experimental conditions.

The effect of the ionic strength can be seen from the following data, obtained at pH 2.14 and 4.19 at constant concentrations of ODA ($4.35 \cdot 10^{-2}M$), boron ($3.41 \cdot 10^{-3}M$) and ND ($5.0 \cdot 10^{-2}M$):

| | | | | | |
|-------------------------|------|------|------|------|------|
| <i>I</i> : | 0.1 | 0.3 | 0.5 | 0.8 | 1.0 |
| <i>E</i> , % (pH 2.14): | 97.2 | 96.1 | 78.1 | 28.2 | — |
| <i>E</i> , % (pH 4.19): | 93.3 | 93.3 | 92.0 | 92.0 | 90.1 |

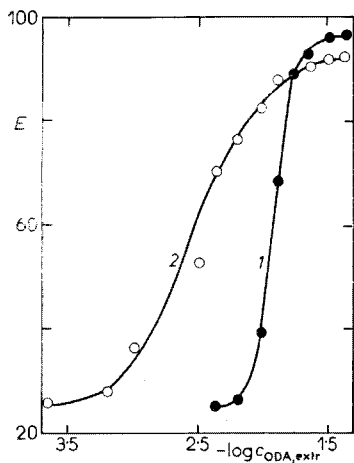


FIG. 7

The Effect of the Concentration of *n*-Octadecylamine on the Percentage Boron Extraction with 2,3-Naphthalenediol in *n*-Butanol
 $c_B = 1.70 \cdot 10^{-3}M$, $c_{\text{ND}} = 1.5 \cdot 10^{-2}M$, I 0.1, $V_{\text{org}} = V_{\text{aq}}$, pH: 1 2.41, 2 4.15.

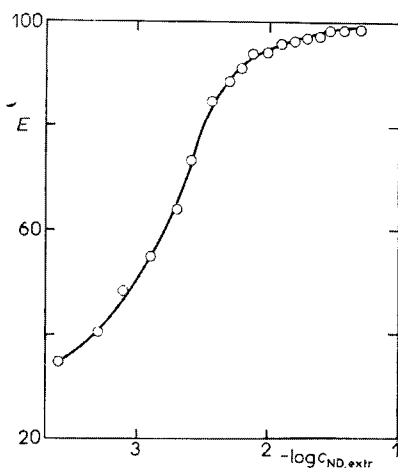


FIG. 8

The Effect of the Concentration of 2,3-Naphthalenediol in *n*-Butanol on the Percentage Boron Extraction in the Presence of *n*-Octadecylamine
 $c_B = 1.70 \cdot 10^{-3}M$, $c_{\text{ODA}} = 4.35 \cdot 10^{-2}M$, pH 2.45, I 0.1, $V_{\text{org}} = V_{\text{aq}}$.

DISCUSSION

The extraction of boric acid from an aqueous solution, in which a solution of ND and either DPG, TPA or ODA in *n*-butanol is used as the extractant, is the result of numerous equilibria. Dissociation of boric acid, formation of polyborates, dissociation of ND, protolysis of the DPG, ODA or TPA cation, formation of ND complexes with boric acid and dissociation of the complex acid formed, formation of the ion-associate from the complex anion and an organic cation, its distribution between the two liquid phases and the distribution of ND and DPG, ODA or TPA probably occur. The appropriate equilibrium constants have not yet been determined for most of these equilibria. For solutions where $c_{\text{ND}} > c_{\text{B}}$ (this condition was satisfied in all our experiments), it can be assumed²⁻⁷ that complex $\text{H}[\text{BL}(\text{OH})_2]$ or, after dissociation, anion $[\text{BL}(\text{OH})_2]^-$ predominates in the aqueous solution. The latter then forms the extractable ion-associate, $\{\text{X}^+, [\text{BL}(\text{OH})_2]^- \}$, with the bulky hydrophobic cation, X^+ .

The influence of the factors which can affect the percentage boron extraction in the form of this ion-associate was investigated. The optimum pH, at which a higher percentage of boron is extracted, differs for different cations (Fig. 1). When DPG or ODA is used, the maximum percentage extraction lies in the pH range from 2 to 2.5; when a TPA salt is employed, it lies at $\text{pH} > 10$. It was found that the $\text{pH}_{1/2}$ value shifts one unit to higher values on a decrease in the DPG or ODA concentration by one order of magnitude (at a constant ND concentration). The $\text{pH}_{1/2}$ value for boron remains unchanged when the ND concentration decreases by one order at a constant concentration of DPG or ODA. These facts can be explained on the basis of the relationship for the boron $\text{pH}_{1/2}$ for the extraction in the presence of DPG or ODA. It is assumed that boron is present in the organic phase in the form of the described ion-associate and in the aqueous phase (at $c_{\text{ND}} > c_{\text{B}}$ and $\text{pH} \approx 2$) predominantly as the non-dissociated acid, $\text{H}[\text{BL}(\text{OH})_2]$. Although the pK_a value for this acid has not been determined, it can be assumed, by analogy with the pK_a values for similar complex boron acids, that $\text{pK}_a > 4$. From the $\text{pK}_a(\text{X}^+)$ values for DPG (10.12) and ODA (10.60) (see ref.⁸), it can be assumed that they are completely converted into cation X^+ at $\text{pH} \approx 2$. The boron distribution ratio, D_{B} , is then given by the expression

$$D_{\text{B}} = \frac{[\{\text{X}^+, [\text{BL}(\text{OH})_2]^- \}]_{\text{org}}}{[\text{HBL}(\text{OH})_2]_{\text{aq}}}, \quad (1)$$

where X^+ denotes the DPG or ODA cation. Using the relationships for the ion-associate stability constant, $\beta_{\text{as}} = \frac{[\{\text{X}^+, [\text{BL}(\text{OH})_2]^- \}]_{\text{aq}}}{[\text{X}^+]_{\text{aq}} \cdot [\text{BL}(\text{OH})_2^-]_{\text{aq}}}$, its distribution constant, $K_{\text{D}} = \frac{[\{\text{X}^+, [\text{BL}(\text{OH})_2]^- \}]_{\text{org}}}{[\{\text{X}^+, [\text{BL}(\text{OH})_2]^- \}]_{\text{aq}}}$ and the dissociation constant of acid $\text{H}[\text{BL}(\text{OH})_2]$, $K_{\text{a}} = \frac{[\text{H}^+]_{\text{aq}} [\text{BL}(\text{OH})_2^-]_{\text{aq}}}{[\text{HBL}(\text{OH})_2]_{\text{aq}}}$, expression (1) can be converted into

$$D_B = K_D K_a \beta_{as} [X^+]_{aq} / [H^+]_{aq} \quad (2)$$

For $\text{pH}_{1/2}$ ($\log D_B = 0$) it holds that

$$\text{pH}_{1/2} = \text{p}K_D + \text{p}K_a - \log \beta_{as} + \text{p}X_{aq}^+ \quad (3)$$

From this relationship it follows that a decrease in the X^+ concentration by one order of magnitude leads to an increase in the $\text{pH}_{1/2}$ value by one unit and that $\text{pH}_{1/2}$ is independent of the ND concentration.

$\text{pH}_{1/2}$ increases by much less on a decrease in the TPA concentration by one order of magnitude than with DPG or ODA. Explanation of this fact requires a quantitative description of boron extraction in the presence of TPA, which is complicated, since at $\text{pH} \approx 10$ the dissociation of boric acid, of ND and of the complex acid play a role, in addition to the above-mentioned equilibria.

The boron extraction recovery increases with increasing ND concentration (Figs 2, 5 and 8) and with increasing concentration of the particular cations (Figs 3, 6 and 7). An increase in the DPG or ODA concentration exerts a greater influence on the percentage boron extraction at lower pH values, as can be seen from Figs 3 and 7 and which also follows from relationship (2), as $[X^+]_{aq}$ is greater at lower pH at the given DPG or ODA concentration. The ND, DPG or ODA concentrations in the extractant can be increased only up to a certain value; when this is exceeded, a solid phase is formed during the extraction. The maximum ND concentration differs for different cations: it is 0.05M for DPG and ODA, and 0.1M for TPA. The highest usable base concentrations in the extractant are $5.02 \cdot 10^{-2}\text{M}$ -DPG, $4.25 \cdot 10^{-2}\text{M}$ -ODA and $1.25 \cdot 10^{-1}\text{M}$ -TPA.

At a certain cation concentration the percentage boron extraction increases with increasing ND concentration up to a molar ratio of $c_{\text{ND}} : c_{\text{B}} = 4$ for DPG and ODA (Figs 2 and 8) and $c_{\text{ND}} : c_{\text{B}} = 2$ for TPA (Fig. 5). The percentage extraction does not increase on a further increase in the ND concentration. If more than 90% recovery is to be achieved in the boron extraction, then c_{DPG} must be $1.25 \cdot 10^{-2}\text{M}$, c_{ODA} $2.2 \cdot 10^{-2}\text{M}$ and c_{TPA} $1.0 \cdot 10^{-2}\text{M}$ at $c_{\text{B}} 1 \cdot 10^{-3}\text{M}$. If the boron percentage should not decrease substantially, then the molar concentrations of ND and DPG in the extractant must be at least five times the original boron concentration in the aqueous phase (Fig. 4).

The effect of the ionic strength (SO_4^{2-}) is marked only with ODA at $I \geq 0.5$, especially at $\text{pH} < 4$. The interference of perchlorate in the boron extraction in the studied system has already been demonstrated¹. The presence of chloride also somewhat decreased the boron percentage extraction. However, if sulphate was simultaneously present, the interference of chloride was not encountered up to a concentration of 100 mg $\text{Cl}^-/1$. PO_4^{3-} and SiO_3^{2-} anions, which can also be encountered during

the determination of boron in plant material, also do not affect the extraction recovery.

It has been found that the temperature (in a range from 10 to 70°C) exerts no significant influence on the completeness of the boron extraction in the studied system.

Under suitable conditions, all three cations used (DPG, ODA and TPA) permit extraction of 96–98% of the boron present in the aqueous phase, using an ND solution in n-butanol. DPG and ODA are advantageous in that the extraction of boron takes place in an acidic medium in their presence. Of the two, DPG is the more advantageous, because of the simpler preparation of the extractant. As follows from Storm's unpublished results⁹, ND alone in hexanol (1M) gives $D_B = 8.13$, so that 89% of the boron is extracted at $V_{org} = V_{aq}$.

On the basis of the results obtained, a solution of 2,3-naphthalenediol and di-phenylguanidine in n-butanol has been selected as the stationary phase for the extraction chromatography of boron.

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