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N,N-*bis*(2,3-Dihydroxypropyl) Octadecylamine for Liquid–Liquid Extraction of Boric Acid

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ABSTRACT

N,N-bis(2,3-dihydroxypropyl) octadecylamine (BPO) has been synthesized by condensation of octadecylamine with 2 M of 1-chloro 2,3-propandiol (1-chloroglycerol) in alcohol, in high yields (88.0%). Its solution in 2-ethyl hexanol has been demonstrated to be very efficient in liquid–liquid extraction of boric acid from aqueous solutions. Two vicinal-diol functions of BPO make it versatile reagent for boron extraction. The long aliphatic chain involved provides solubility in organic solvents. At relatively low boric acid concentrations, i.e., 1.2% (w/w), about 98% of BPO involves boron chelation, in nonbuffered conditions. The role of the tertiary amine function is entrapping acidic proton resulting from possible anionic borate complexation. In the study, pH dependence of the boric acid extraction and regeneration conditions of the chelating agent has been investigated. Overall results indicate that the boron complex is stable above pH 4.7 and the presence of some common

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foreign ions such as Ca(II) and Mg(II) does not affect the extraction. The complexed boron can be recovered from organic phase by treating with 2 M H_2SO_4 solutions. Due to nonhydrolyzability of the linkages in BPO it can be recovered and may be of interest to use in continuous extraction systems.

Key Words: Boron extraction; Liquid–liquid extraction; Boric acid; N,N-bis(2,3-dihydroxypropyl) octadecylamine.

INTRODUCTION

Separation, especially selective separation is one of the most important tasks both in chemical industry and laboratory. Among the separation techniques, liquid–liquid extraction is still an important process because of its time saving and cost-effective nature. Supercritical gas extraction is a new developed version of liquid–liquid extraction.[1] However its use is somewhat limited due to difficulties in pressure equipments and its main applications have been confined mostly to extraction of biologically active chemicals, at least for the time being.[2] Another version of the liquid–liquid extraction is chelate extraction in which an organic-soluble chelating agent extracts the solute, rather than direct extraction by an organic solvent. Presumably regenerability of chelating agent is the most important criteria for application in large-scale continuous processes, beside high solubility of chelating agent (in free and chelated forms) in water-immiscible organic solvents.

In order to meet these requirements, synthesis of new designed chelating agents seems to be essential. In conjunction with these considerations we have synthesized a new boron-selective chelating agent N,N-bis (2,3-dihydroxy propyl) octadecylamine (BPO). Two vicinal-diol functions in the molecule serve complexation with boric acid. Similarly sugar derivatives such as d-sorbitol and mannitol are useful compounds for complexation with boric acid and borates.[3] Based on this fact a boron specific resin obtained by modification of chloromethylated polystyrene resin with N-methyl d-glucamine functions emerged in the mid-1960s.[4] Since presence of boron in irrigation water causes plant stunning, its removal is especially important in an agricultural viewpoint.[5] Although cellulose[6] and magnesium hydroxide[7] have been used to extract boric acid from aqueous solutions, these are not efficient for low concentrations in ppm levels. In a recent study, polyepicholorohydrin modified with N-methyl d-glucamine has been used in liquid membrane for boron removal.[8] In our previous study we have

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demonstrated that sorbitol-modified poly (N-glycidyl styrene sulfonamide) is a regenerable boron specific sorbent.[9]

There are few reports in the literature dealing with liquid–liquid extraction of boric acid. In those studies generally 1,2 or 1,3 diols with relatively long aliphatic chains have been used for boron extractions.[10,11] In a similar study 2-butyl 2-ethyl 1,3-propandiol has been shown as a boron-chelating agent with reasonable efficiency.[12] Recently a tertiary amine function has been demonstrated to be essential for an efficient boron extraction because of its neutralizing effect on the proton formed during the boron complexation.[13]

In the present study boron extraction ability of N,N-bis (2,3-dihydroxypropyl) (BPO) possessing two vic-diole functions has been investigated. pH-dependence of liquid–liquid extraction and interferences of some common metal ions such as Ca(II), Mg(II), and Fe(III) have also been studied.

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EXPERIMENTAL

2-Ethyl hexanol was distilled before use. All the other chemicals used were analytical grade commercial products, octadecylamine, 1-chloroglycerol (Fluca), H_3BO_3 (Carlo Erba). They were used without further purification. NMR spectra were taken using a Bruker 250MHz NMR Spectrometer.

IR spectrum was recorded by Mattson 1000 FT-IR Spectrometer. Elementary microanalysis was performed by Carlo-Erba 1106 elemental analyzer.

Boric acid determinations were carried out by titration with 0,1 M NaOH solution in the presence of 0,4 M d-sorbitol as described in the literature.[14]

Synthesis of N,N-bis(2,3-Dihydroxypropyl) Octadecylamine (BPO)

Octadecylamine (16.2 g, 0.06 mole) was dissolved in 40 ml ethanol. To this solution 10 ml (0.12 mole) 1-chloro 2,3 propane diol, 1-chloroglycerol was added and the solution was refluxed for 72 h. To neutralize the HCl formed, the solution of 6.8 g (0.12 mole) KOH in 20 ml ethanol was added to the mixture in four portions in 12-h time intervals. Then, the mixture was filtered and washed with 20 ml of hot ethanol. The filtrate was refluxed in the presence of 20 g solid potassium carbonate to remove trace water and filtered. About three-fourths of the filtrate was evaporated by a rotavapor and left to stand for 2 h. The white crystalline mass was filtered and dried under vacuum

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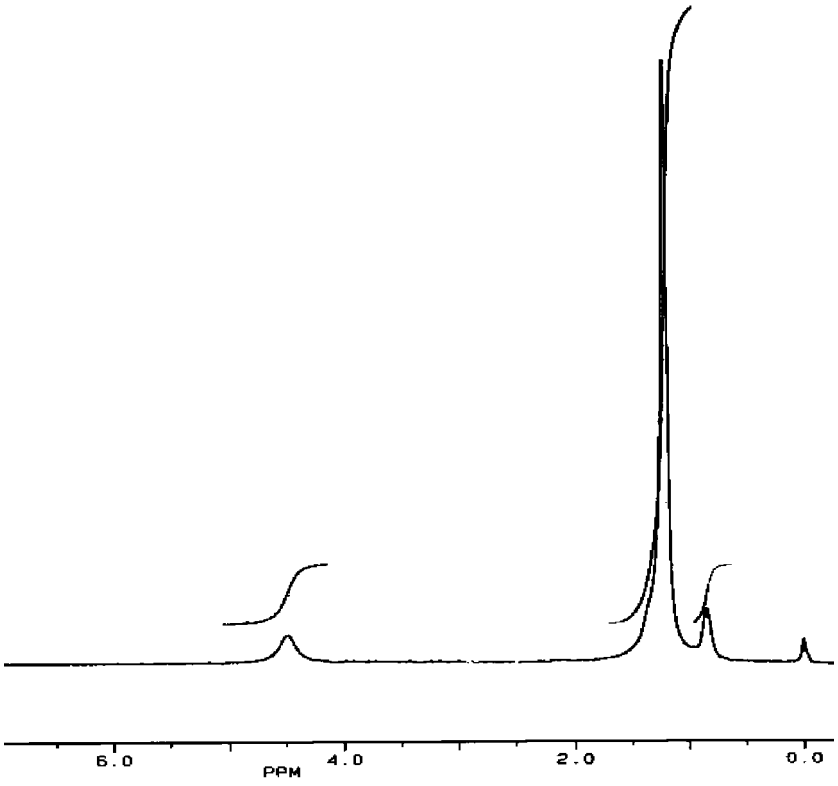

Figure 1. ^{1}H-NMR spectrum of N,N-bis(2,3-dihydroxypropyl) octadecylamine (BPO) in DMSO-d_6.

for 24 h at 40°C. Yield 22.7 g (88.0%) mp: 58.5°C. Elementary microanalysis: Calculated % (found); C: 69.06% (68.9), H: 12.23% (11.75), N: 3.35% (3.10). The product is soluble in many hydrocarbon solvents such as 2-ethyl hexanol, cyclohexanol, hot ethanol, $CHCl_3$ and insoluble in water. ^{1}H-NMR spectrum of the product is given in Fig. 1.

Determination of the Protonation Constant of BPO

Since the boron complexation of BPO is competitive with its protonation, determination of the protonation constant might be necessary to predict extent of the extraction. This was carried out in the extraction conditions as follows:

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10 ml of the organic solution of BPO (0.0923 M) was added to 10 ml distilled water. The mixture titrated potentiometrically under continuous stirring.

$$[BPO]_{org} + [HX]_{aq} \overset{K_p}{\rightleftharpoons} [BPO{-}H^+]_{org}X^- + H_2O$$

$$K_p = \frac{[BPO{-}H^+]_{org}X^-}{[BPO]_{org}[HX]_{aq}} = K{\cdot}K' \quad (1)$$

Based on pH-titrant plot, the protonation constant, K_p of the following equilibrium was calculated as usual. Since $[BPO{-}H^+]X^-$ represents protonated portion of BPO, it can be calculated based on initial acid concentration and the acid concentration obtained by pH measurement. From the experimental data the average value of K_p was calculated as $9.2 \pm 0.16.10^{+4}\,L\,mol^{-1}$.

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Boric Acid Extraction

BPO 20.86 g (0.05 mol) was dissolved in 2-ethyl hexanol and the solution was made up of 500 ml (0.1 M solution). Ten milliliters of the organic solution was mixed up with 10 ml aqueous H_3BO_3 solution (0.1 M). The mixture was shaken vigorously in a reparatory funnel, using Heidolp Unimax 1010 model shaker for 10 min. Then it was allowed to stand for separation of the two phases (about 15 min). 5 ml of aqueous phase was taken in 20 ml of 0.1 M of d-sorbitol solution and 2 drops of phenolphthalein solution (0.1 M) was added to the solution. This solution was titrated with 0.1 M NaOH solution until it was the pink color of the indicator. Thus, consumption of 1.80 ml NaOH solution corresponds to 0.036 M concentration of the residual boric acid. The difference leads to 0.64 mmol, which is extracted by the 10 ml of the organic solution. In other words the distribution coefficient of the extraction in this case is:

$$K_D = C_{org}/C_{aq} = 0.064/0.036 = 1.78 \quad (2)$$

Regeneration of BPO and Recovery of Boric Acid from the Extract Phase

Five milliliters of the above extract phase was taken and interacted with 5 ml of 2 M H_2SO_4 solution. The mixture was shaken for 15 min and 0.25 g NaCl was added to speed up phase separation. Then 4 ml of the acid solution was separated and diluted to 10 ml. This solution was titrated with 0.1 M

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NaOH solution using phenolphthalein color indicator. At the end of neutralization of the sulfuric acid, 20 ml of d-sorbitol solution (0.4 M) was added and titration was continued until appearance of characteristic pink color of the phenolphthalein in basic media. 2.52 ml of additional NaOH consumption indicates 0.3155 mmol of boric acid extracted by 5 ml of the organic the solution.

The chelating agent becomes boron-free by acid treatment as described above. After this process the amino group of BPO must be converted into ammonium hydrogen sulfate. To obtain the chelating agent in free amine form the above organic phase was separated and shaken with 5 ml of 1 M NaOH solutions. The resulting organic solution at this stage became regenerated. Boron uptake ability of the regenerated solution was tested by a similar loading experiment.

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pH and Concentration Dependence of the Boric Acid Extraction

Having basic amine function, the chelating agent PBO is expected to gain some solubility, especially in acid media. In order to investigate the effect of pH and concentration, boron uptake experiments were repeated at different pHs (using pH: 1.56 sodium citrate–citric acid, pH: 3.63, 4.10, 4.48, 5.00, 5.56 acetic acid–sodium acetate, pH: 5.86 $NaHPO_4$–KH_2PO_4 buffer solutions) and in different concentrations. The data collected were used to build Fig. 2 and Fig. 3, respectively.

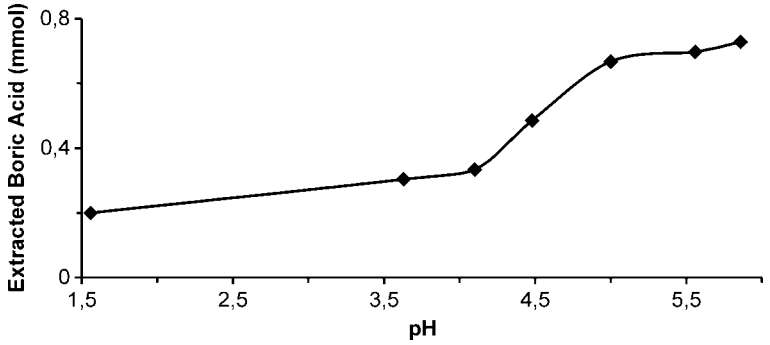

Figure 2. pH dependence of the boric acid extraction, by 10 ml BPO solution (0.1 M). from 10 ml aqueous H_3BO_3 solutions (0.1 M) at different pHs.

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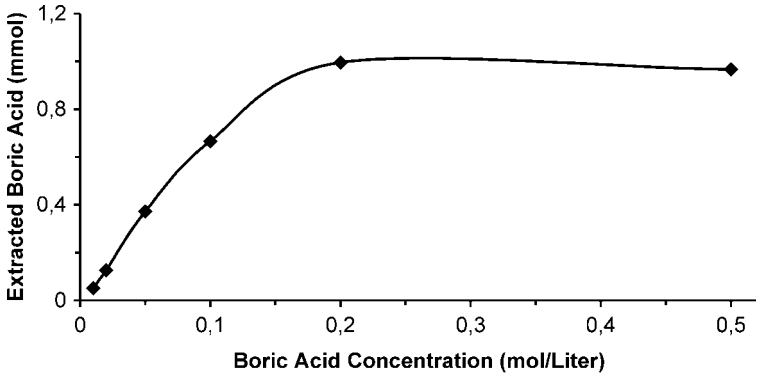

Figure 3. Concentration dependence of the boric acid extraction. The amount of boric acid extracted by 10 ml of BPO solution (0.1 M) from 10 ml aqueous H_3BO_3 solutions in various concentrations.

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Estimation of the Solubility of BPO in Water

In order to estimate extent of leakage of BPO during the boric acid extraction process its solubility was determined roughly by conductometric method as follows: 10 ml of organic solutions containing BPO (0.1 M) was shaken with 10 ml of distillated water. After equilibrium was established, 8 ml of aqueous phase was separated and mixed up with 2 ml H_2SO_4 solution (0.1 N). The solution was titrated conductometrically with 0.05 M NaOH solutions. From the titration curve maximum solubility was estimated roughly as 0.5 mg per liter of water.

RESULTS AND DISCUSSION

The whole study consists of two main steps: 1) Synthesis of N,N-bis (2,3-dihydroxy propyl) octadecylamine (BPO); 2) Testing its ability in liquid–liquid extraction of boric acid.

BPO was synthesized by alkylation of octadecylamine with monochloroglycerol (Hoffmann Alkylation) as depicted in Scheme 1.

High yields have been attained by portion-wise addition of KOH in alcohol to the mixture while refluxing. The resulting product is a low melting compound (mp: 58.5°C) and soluble in water-immiscible organic solvents such as 2-ethyl hexanol and cyclohexanol. Elementary microanalysis and ^{1}H-NMR spectrum (Fig. 1) of the product confirm the proposed structure.

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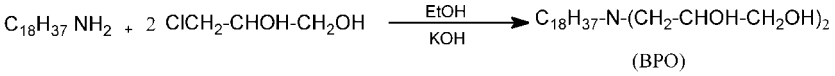

Scheme 1.

Thus, aliphatic protons appear at 0.85–1.23 ppm range. The broad signal at 4.5 ppm represents OH protons of the molecule. Disappearances of that signal with D_2O exchange and integral ratio 12/1 of the two signal groups are clear-cut evidences for the proposed structure.

Although its FT-IR gives no further information (due to the fact that OH stretching vibrations observed at 3250–3600 cm^{-1} range obscure the N—H vibration bands expected at the same region) intensity of this broad band can be ascribed to the formation of the expected structure. The strong band at about 1650 cm^{-1} must be due to plane-bending vibrations of the OH groups.

This compound, BPO has been designed so as to be a perfect chelating agent for liquid–liquid extraction of boric acid. The two vic-diole functions involving are expected to chelate boric acid tightly. The tertiary amino function must provide entrapping of the proton resulting from formation of tetra borate complex. Long aliphatic chain makes BPO and its boron complex soluble in organic solvents. On the other hand, structurally, this compound does not have hydrolyzable linkages. This point is crucial for regeneration of the chelating agent by acid–base treatments in recycling.

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Liquid–Liquid Extraction of Boric Acid

In order to test boron uptake ability of BPO its 0.1 M solutions in 2-ethyl hexanol were mixed up and shaken with boric acid solutions in different conditions. After separation of the organic phases, residual boron concentration in the refinate phase was determined by titration with NaOH solution in the presence of d-sorbitol. Extracted boron was assayed based on the difference of boric acid contents of the initial and final solutions. The boric acid extraction can be represented simply as shown in Scheme 2.

The overall equilibrium constant (K) of the boric acid in the extraction conditions;

$$K = \frac{[BPO{-}B]_{org}}{[BPO]_{org}[B]_{aq}} \tag{3}$$

(Let, $[H_3BO_3] = [B]$)

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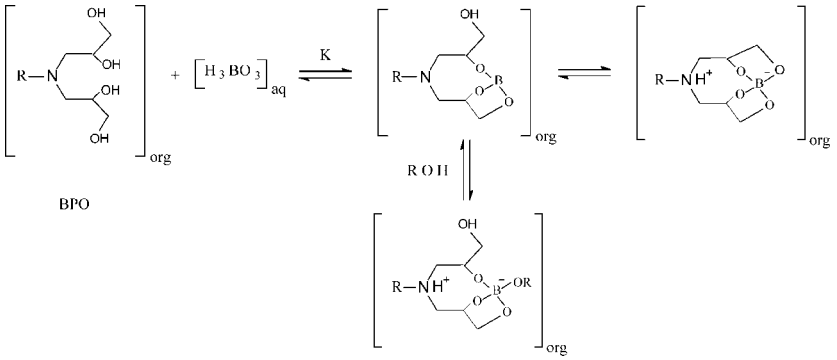

Scheme 2.

In fact boron complexation of BPO must be much more complicated than pictured in Scheme 2. Since the vic-diol group on each propanediol function might be in transconfiguration, formation of neutral boron ester seems be favorable. Moreover, tetra-coordinated anionic borate formation might also be possible by incorporation of 2-ethyl hexanol (solvent). However a strong chelation via formation of tetra coordination by BPO can also be considered, because the energy loss for such a structure can be compensated by additional chelate ring formation and entropy gain. In fact 1:1 diol–boron complexes might be expected to be less favored in comparison to 2:1 complexes as it has been proved on boron–sugar complexes.

The distribution constant K_D of boron extraction;

$$K_D = [\text{Boron in organic phase}]/[\text{Boron in water}]$$

$$= [\text{BPO–B}]/[\text{B}] = 1.78$$

In the case of equal volumes of organic and aqueous solutions, the distribution coefficient is $K_D = 1.78$.

By definition the extraction coefficient is;

$$G = \frac{[\text{BPO—B}]_{org} V_{org}}{[\text{BPO—B}]_{org} V_{org} + [\text{B}]_{aq} V_{aq}}$$

Since $V_{aq} = V_{org}$;

$$G = K_D/(1 + K_D) = 0.64 \pm 0.03$$

which means 64.0% of 0.1 N H_3BO_3 is being extracted by 0.1 M organic BPO solutions in each contact.

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The regeneration by the acid treatment takes place via acid catalyzed decomplexation of boron. It can be represented as

$$[\text{BPO—B}]_{org} + [\text{HX}] + 3\text{H}_2\text{O} \overset{K'}{\rightleftharpoons} [\text{BPO—H}^+]_{org}\text{X}^- + [\text{H}_3\text{BO}_3]_{aq} \quad (4)$$

The decomplexation constant

$$K' = \frac{[\text{BPO—H}^+]\ {}_{org}\text{X}^-}{[\text{BPO—B}]_{org}[\text{HX}]} \quad (5)$$

Since protonation of BPO is a competitive reaction in the extraction, it must be taken into consideration as well. The protonation of BPO

$$[\text{BPO}]_{org} + [\text{HX}]_{aq} \overset{K_p}{\rightleftharpoons} [\text{BPO—H}^+]_{org}\text{X}^- + \text{H}_2\text{O} \quad (6)$$

$$K_p = \frac{[\text{BPO—H}^+]_{org}\text{X}^-}{[\text{BPO}]_{org}[\text{HX}]_{aq}} = K \cdot K' \quad (7)$$

The decomplexation constant K' can be calculated directly by Eq. (7).

$$K' = K_p/K = 8.08 \cdot 10^4/49.4 = 1.6 \cdot 10^3.$$

From Fig. 2, it is clearly seen that decomplexation of boron takes place at pHs lower than 4.70. In other words the boron complex or complexes are stable in neutral or faintly basic media. Slight jump at about pH = 5.8 can be ascribed by formation of anionic borate complex beyond this point. When pH > 5, the hydrogen ion concentration can be neglected and the reaction (4) becomes less favored. In that case, the reaction in Scheme 2 alone becomes predominant. Experiments with various boron concentrations indicate that the equilibrium extraction constant of boric acid is $49.4\,\text{mol}^{-1}\,\text{L}$. Figure 3 implies that boron extraction capacity approaches the theoretical capacity when boric acid concentration is higher than $0.2\,\text{mol}\,\text{L}^{-1}$.

Extracted boron calculated, by using $K_D = 1.78$, well matches with the quantities shown in Fig. 3. For instance, in the extraction from 0.1 M H_3BO_3, the Eq. (2) yields;

$$K_D = [\text{BPO—B}]/[\text{B}] \rightarrow 1.78 = x/(0.1 - x) \quad \text{gives } x = 0.064\,\text{mol}\,\text{L}^{-1},$$

where x denotes the boron concentration in organic phase. Since the volume of organic phase is 10 ml, the extracted amount is 0.64 mmol, which is almost the same with the observed value.

It is interesting to note that, in the nonbuffered boric acid experiments, slight differences were observed in pH values before and after the boron

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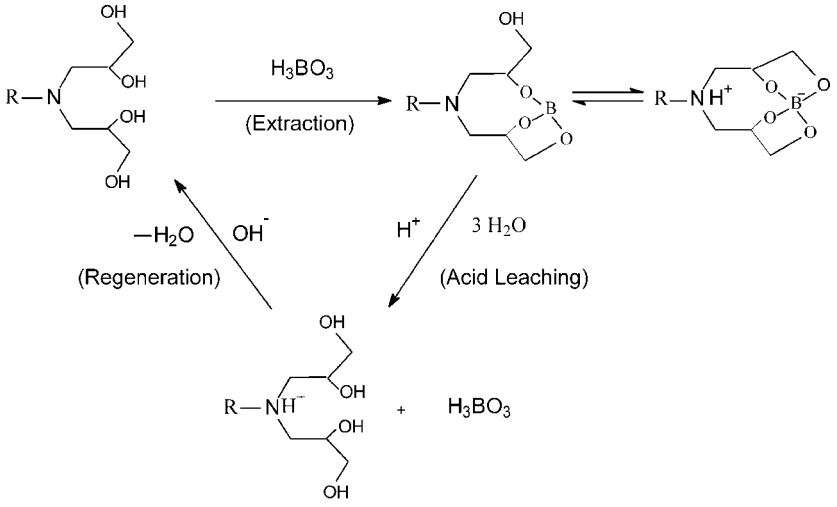

Scheme 3.

extraction (i.e., pH from 6.1 to 5.9). This must be due to small dissociation of ammonium cation yielding proton. This assumption is inconsistent with the slight increase in extracted boron when pH $>$ 5.8 (Fig. 2). Redistribution of the released proton between the two phases results in slight decrease in the pH value of the aqueous solution.

Interference

In order to examine any probable interferences of foreign ions, the extraction experiments were repeated in the presence of 0.1 M Ca(II), Mg(II), and Fe(III) ions. The experiments were conducted in nonbuffered conditions. In the cases of Ca(II) and Mg(II) ions no interferences were detected. However $Fe(OH)_3$ precipitation was observed when 0.1 M Fe(III) was used and the amount of extracted boron was about 0.52 mmol by 10 ml of BPO solution. The difference from the original value (0.64 mmol) is 0.12 mmol. This result clearly implies that an appreciable interference comes from ferric ions. Nevertheless in practice presence of Fe(III) ions at such a high concentration is not common.

This result obtained shows some advantageous over boron extractants reported before. According to the literature[15] extraction from 0.1 M H_3BO_3 solutions by diols having less than 6 and more than 12 carbon atoms show

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smaller distribution coefficients (between 0.015–1.45). Diols with 8,9-carbon atoms exhibit comparable or higher distribution coefficients (2–11.3), in the extraction from 0.1 M H_3BO_3 solutions. However those materials such as 2-ethyl 1,3-hexan diol (efficient one) suffer from appreciable amounts of leakage (0.5%–2.6%) into aqueous phase.

In conclusion, the extraction process presented seems to be a feasible route for removal of boron from aqueous solutions. Full scheme of the extraction and regeneration steps can be depicted as shown in Scheme 3.

Apparent advantages of the process are as follows.

(i) The chelating agent has reasonable efficiency in boron extraction.
(ii) The distribution coefficient is 1.78%. Hence, the extraction system can be regarded as a feasible method for large-scale boron extractions.
(iii) The chelating agent does not have hydrolyzable groups, and it can be regenerated by 2 M H_2SO_4 solutions, without loosing its activity.
(iv) Presence of Ca(II) and Mg(II) ions does not induce any interference in the extraction process. Slight interference of 0.1 M Fe(III) solution may not bring difficulties in practice, owing to the fact that this ion does not present in such a high concentrations.

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