REVIEW

Advances in Boron Isotope Separation by Ion Exchange Chromatography

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Boron isotope separation by ion exchange chromatography is characterized by high efficiency, low energy consumption, safe operation and low equipment investment. It is a promising process for industrial scale production. The latest progress for enriching ^{10}B isotope by ion exchange chromatography is reviewed in this article. Currently, strongly basic anion exchange resins, weakly basic anion exchange resins and boron-specific resins are used as chromatographic column packing materials. With a brief introduction of the separation principle, the advantages and disadvantages of these resins are compared. Some elements influencing the single-stage separation factor are also discussed.

Keywords: Boron, Isotope separation, Ion exchange chromatography, Separation factor.

INTRODUCTION

Boron has two stable isotopes (^{10}B and ^{11}B) with a relative abundance of 19.8 % and 80.2 %, respectively[1]. ^{10}B has a thermal-neutron capture cross-section (3837 barns) of as large as five times that of natural boron and 7.7×10^5 times that of ^{11}B[2]. Therefore, ^{10}B is generally used for control rods, neutron detectors in nuclear industry and for cancer therapy in medical field[3,4]. For efficient control and to have a compact core size of fast reactors, it is required to use highly enriched boron in ^{10}B isotope[5].

The main methods for boron isotope separation are chemical exchange distillation[6], fractionation of BF₃[7], laser separation[8] as well as ion exchange chromatography. Among these methods, chemical exchange distillation has been applied in industrial scale production of boron isotopes. However, it has shortcomings of large investment in equipment and complexity of operation. Compared with other methods, ion exchange chromatography is characterized by high efficiency, low energy consumption, safe operation and low equipment investment. It will be one of the most promising processes for boron isotope separation.

Principle of boron isotope separation by ion exchange chromatography: Boron isotope separation by ion exchange chromatography is based on the ion exchange reaction between the solution phase and the resin phase. The main operating process is as follows: (A). Boric acid is fed continuously to the top of the ion exchange column; (B).The band is then developed by an adequate eluent after the resin is saturated with the feed solution. As band development proceeds, the lighter isotope ^{10}B is enriched in the rear band and the heavier isotope ^{11}B in the front; (C). Once the isotopic mole fraction of ^{10}B at the rear of the band reaches the value required, it can be withdrawn from this end[9].

The separation mechanism is basically the same for different kinds of resins. The most important boron isotope exchange between $B(OH)_3$ in the solution phase and $B(OH)_4^-$ in the resin phase is described by the reaction:

$$^{10}B(OH)_3 + {}^{11}B(OH)_4^- \rightarrow {}^{11}B(OH)_3 + {}^{10}B(OH)_4^-$$
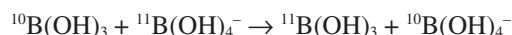
with an isotopic equilibrium constant defined by:

$$K_B = [^{11}B(OH)_3][^{10}B(OH)_4^-]/[^{10}B(OH)_3][^{11}B(OH)_4^-]$$

The earliest estimate for K_B (K_B = 1.0194 at 25 °C) is reported by Kakihana *et al.*[10]. Although the value is widely cited, recent assessments indicate that K_B may be significantly larger: K_B = 1.033 (Ref. 11); K_B = 1.0260 (Ref. 12 and 13); K_B = 1.0267 (Ref. 14); K_B = 1.0285 (Ref. 15). The equilibrium constant (K_B) is larger than unity, which means the heavier isotope is preferentially fractionated into the boric acid and the lighter one into the borate anion.

The single-stage separation factor (S) is the most fundamental physicochemical property in the boron isotope separation process. It is defined as:

$$S = [^{10}B/^{11}B]_{resin}/[^{10}B/^{11}B]_{solution}$$

During the ion exchange separation process, ^{10}B is fractionated in a boron complex with a tetrahedral coordination geometry in resin phase more selectively than that with a trigonal planar geometry in solution phase, while ^{11}B exhibits the opposite relation[16]. Since the S value is close to unity, the adsorption band has to be displaced over a long distance to achieve a high degree of enrichment[17].

Progress in enriching ^{10}B by ion exchange chromatography

Strongly basic anion exchange resins: Yoneda *et al.*[18] first reported a study of boron isotope separation by using a strongly basic anion exchange resin Amberlite CG-400 I in 1959. The S value obtained was 1.016. Kakihana *et al.*[10] obtained an S value of 1.019 by Diaion PA312 resin. Sharma *et al.*[5] obtained an S value of 1.027 by Tulsion A-36 MP (a type II resin).

In 1971, a French company, Isobor, exploited a plant, yielding 200 kg of ^{10}B with concentration of 90 % and 800 kg ^{11}B annually by Amberlite IRA-410 resin[3].

The system with strongly basic resins has a relatively large separation factor, but it has a disadvantage of complicated post-treatment operation. Generally, post-treatment procedures for strongly basic resins consist of two main steps, elution by a certain acid, such as HCl and H_2SO_4, and regeneration by basic regenerant, typically, NaOH[19]. The regeneration process requires a large amount of NaOH. The complexity of the post-treatment has hampered the development of strongly basic resins in boron isotope separation.

Weakly basic anion exchange resins: The separation mechanism of weakly basic anion exchange resins is generally considered to be boron isotope exchange reaction. But Huang *et al.*[20] believe that the boron separation is based on nonionic interaction rather than ion exchange reaction between boric acid and the functional group.

The system with weakly basic anion exchange resins has a benefit of simplified operation in the chromatographic process: boron is eluted out by pure water. In this method the resin is reloaded with boric acid without any regeneration operations[21]. But the S value achieved is relatively small, around 1.01[22]. Now we introduce some separation researches by using weakly basic resins.

Sakuma *et al.*[23] used Diaion WA-21 resin (80-100 mesh) to separate boron isotopes. Three columns (each 21 mm in diameter, 1 m in length) were used. The maximum enrichment of ^{10}B reached 91 % at a migration distance of 256 m. The process was carried out at 40 °C. The feed solution was 0.1M boric acid.

Aida *et al.*[24] also used Diaion WA-21 resin (60-80 mesh) to separate boron isotopes. Eight glass columns (each 30 mm in diameter, 2.1 m in length) were used. The maximum enrichment of ^{10}B reached 98.43 % at a migration distance of 620 m. The process was carried out at 40 °C. The feed solution was 0.1 M boric acid.

Mardan[25] used simulated moving bed (SMB) chromatography. The experiment was performed on a 38 % quaternized 4-vinylpyridine-divinylbenzene resin. A loop of four glass columns, each 22 mm in diameter and 1m in length was used. The continuous separation of boron isotopes by SMB was achieved by simulating countercurrent flow through switching

the inlet and outlet of the fluid periodically. The maximum enrichment of ^{10}B reached 94.15 % at a migration distance of 40 m. The process was carried out at 25 °C. The feed solution was 0.1 M boric acid with 0.2 M mannitol.

A process for ^{10}B enrichment by moving bed was introduced in Patent JP2021925[26]. Ion-exchange resins were supplied to the top of an exchange tower to form a downward moving bed, allowing the aqueous boric acid solution to ascend in the tower, and bringing the solution into contact with the resin.

Patent US5443732[27] disclosed a process and apparatus for the continuous separation of ^{10}B in a continuous annular chromatography (CAC). The processs is shown in Fig. 1. Weakly basic resins were filled in the space between the two concentric cylinders. Boric acid solution and water eluent were fed at a location on the top of the column continuously when the cylinder was rotating. Separated ^{10}B and ^{11}B fractions were continuously collected at different annular displacement along the length of the ion exchange column.
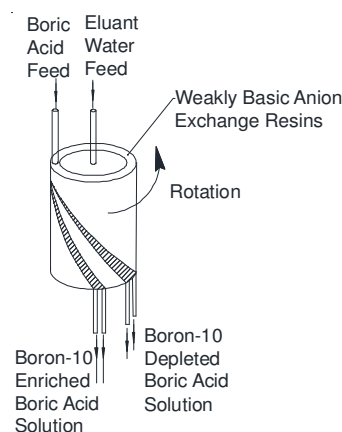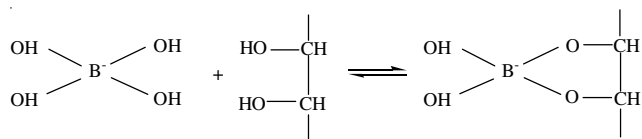

Fig. 1. Continuous annular chromatography processs for boron isotope separation

Boron-specific ion exchange resins: The principle of boron-specific resins (BSRs) is the use of esterification reactions, as shown in the following equation. Borate ions react with polyol parts of the resins to form a variety of borate esters.

Regarding commercially available boron-specific resins, these resins have a macroporous polystyrene matrix, on which N-methyl-D-glucamine functional groups are attached[19]. The functional group has a tertiary amine end and a polyol end. The role of the tertiary amine in the functional group is to neutralize the proton brought by the formation of tetra borate complex. As far as hydroxyl groups are concerned, there are 5 hydroxyl groups in N-methyl-D-glucamine. This allows the formation of a strong complex with boron and improves the possibility of complexation by offering several sites for boron.

Oi *et al.*[22] used Diaion CRB 02 resin and Amberlite IRA 743 resin (Fig. 2) to separate boron isotopes. The S values obtained were 1.018-1.022 at 25 °C. Sonoda *et al.*[16] also investigated the separation performance of N-methyl-D-glucamine

resins in aqueous solution system. The S value obtained was 1.027. These S values indicate that N-methyl-D-glucamine resin has a high selectivity for ^{10}B isotope.
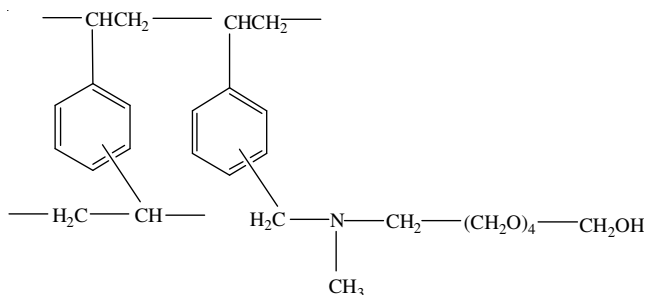

Fig. 2. Structure of Diaion CRB 02 and Amberlite IRA 743 resins

From the standpoint of the separation factor, boron-specific resins are better column packing materials for the chromatographic separation of boron isotopes.

Factors influencing the separation factor

Temperature: Oi *et al.*[22] used Amberlite IRA 743 to separate boron isotopes. The separation factors for 25 °C and 50 °C were 1.022 and 1.020, respectively. The contrast indicates that a lower temperature tends to yield a larger S value. This is consistent with the theory of equilibrium isotope effects. However, a low temperature can result in a slow isotope exchange reaction rate, and is also bad for the elution of ^{10}B from the resin. In general, the process is carried out at room temperature.

Concentration of boric acid: Kakihana *et al.*[10] used Diaion PA312 resin to separate boron isotopes at various boric acid concentrations. The separation factors for 10, 100, and 501 mM were 1.019, 1.010 and 1.007, respectively. It is obvious that the S value in boric acid solutions decreases with increasing concentration.

In a concentrated boric acid solution, there are not only monomeric boron species, $B(OH)_3$ and $B(OH)_4^-$, but also polyborate anions (such as $B_3O_3(OH)_4^-$, $B_3O_3(OH)_3$, $B_2O(OH)_5^-$, $B_2O(OH)_4$). As can be seen from Fig. 3, the polyborate anions contain not only the $B(OH)_4^-$ structure but also the $B(OH)_3$ structure[28]. The formation of polyborate anions in the resin phase accounts for the reduced S value. The concentrations of the polyborate anions depend on, among others, the concentration of boric acid and pH of the solution[29]. A higher boric acid concentration results in more polyborate anions. So a low boric acid concentration seems reasonable. But a very low concentration of boric acid is uneconomical due to a waste of eluent. The most suitable concentration of boric acid is considered to be 0.1 M.
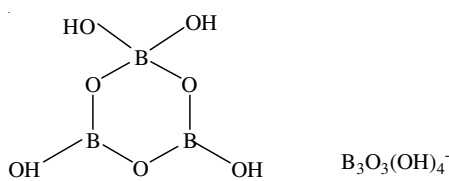

Fig. 3. Structure of polyborate anion $B_3O_3(OH)_4^-$

pH of solution phase: Sonoda *et al.*[16] conducted experiments about pH-dependence of boron isotope separation with N-methyl-D-glucamine resin (MGR) in aqueous solution systems. The result can be seen from Fig. 4. For pH values less than 7, the separation factors were 1.027. For the pH values greater than 11, the factors were 0.998, revealing no fractionation of boron isotopes. In the intermediate pH range, the factors were decreased significantly with an increase in pH. Therefore, weakly acidic solution is beneficial for obtaining a larger separation factor.
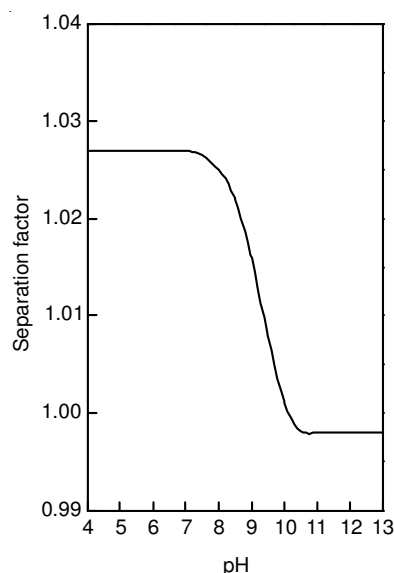

Fig. 4. Effect of pH on separation factor with N-methyl-D-glycamine resin in aqueous solution systems

Pressure: The S value decreases with increasing pressure. As can be seen from Table-1, the S value at high pressures are smaller than the value obtained by using the same chromatographic method at low pressures. This can be explained by the incorporation of $B(OH)_3$ into the resin phase at high pressures *via* the formation of polyborate anions.

TABLE-1
BORON SEPARATION FACTORS OBTAINED BY STRONGLY BASIC ION EXCHANGE CHROMATOGRAPHY AT VARIOUS PRESSURES AND BORON CONCENTRATIONS

Adsorbent	[B] (mM)	Pressure (Mpa)	S	Ref.
Diaion PA312	10	0.1	1.019	10
Dowex 1	10	0.1	1.018	10
Muromac 1 × 8	9.28	2.0	1.013	30
Muromac 1 × 8	0.10	5.0	1.018	31
Muromac 1 × 8	0.10	17.0	1.012	31

Glycol or polyols: S (I, 0.03M $B(OH)_3$) = 1.010, and S (II, 0.1 M $B(OH)_3$ with glycerine (8 wt. %) = 1.016[18]. As mentioned above, the S value increases with decreasing concentration. The difference between the S values of I and II is probably related to the presence of glycerine. Sharma *et al.*[32] explained that glycol or polyols can form complexes with boric acid accompanying with the release of H^+ ions, increasing the acidity of boric acid solutions, which accounts for the difference in S-values.

As shown in Fig. 5 , the separation factor increases as the mannitol to boron ratio is increased from 0 to 2.0. While no appreciable effect is observed by increasing the concentration

of mannitol beyond this value. These behaviors may be attributed to the tendency of mannitol to form 1:1 and 1:2 mole ratio complexes of boric acid with mannitol by decomposing polyborate anions.
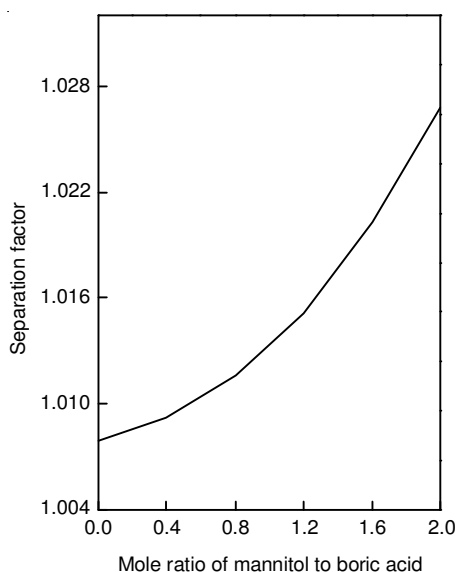

Fig. 5. Effect of mannitol to boric acid mole ratio on separation factor using Tulsion A-36 MP

Form of the resins: Oi *et al.*[22] investigated the dependence of S value on the forms of the resins (free base *vs.* sulfate) at 25 °C. For Diaion CRB 02 resin, the separation factors for free base and sulfate resins were 1.021 and 1.018, respectively. It indicates that the resin in the free base form has a larger separation factor than the resin in the sulfate form. This is due to the difference in pH in the resin phase between the free base and sulfate forms; the pH value in the resin phase is expected to be higher for the free base form resin than for the sulfate form resin, and it is well known that esterification of the borate ion with a polyol is in general promoted at a high pH value. The resin in the free base form shows a better boron separation performance.

Conclusion

Boron isotope separation by ion exchange chromatography is characterized by high efficiency, low energy consumption, safe operation and low equipment investment. A maximum separation factor obtained is 1.027. It may be possible to substitute chemical exchange distillation for boron-10 separation. But further studies should be carried out not only to acquire fundamental knowledge, but also to find a feasible separation process for industrialized production. Continuous operation through combination with other chromatographic methods, such as SMB and CAC, will be a promising direction. In addition, novel resins with better selectivity and larger separation factors should be developed in the future.

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