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Enrichment of Boron-10 by Inverse-Frontal Chromatography Using Quaternized 4-Vinylpyridine–Divinylbenzene Anion-Exchange Resin

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ABSTRACT

In order to enrich ^{10}B, 40 meter band migration of boric acid–mannitol with hydrochloric acid solution was performed by inverse frontal chromatography on a porous, 25% crosslinked, 38% quaternized 4-vinylpyridine–divinylbenzene resin. The maximum enrichment (R_L) of ^{10}B was 94.15%. The overall process parameters, namely slope coefficient (k) and separation coefficient (ϵ), were found to be 0.1282 cm^{-1} and 0.02967, respectively.

INTRODUCTION

Boron is known to have two stable isotopes, ^{10}B and ^{11}B. The natural abundance of ^{10}B is 19.85 atom percent. The thermal neutron absorption cross-sections of ^{10}B and ^{11}B are 3837 and 0.005 barn, respectively, whereas natural boron has an absorption cross-section of 752 barns. Because of the higher absorption cross-section of ^{10}B, boron enriched in ^{10}B is used in the nuclear industry.

Ion-exchange chromatography is one of the most promising processes for boron isotope separation, and it has been used for the separation of boron isotopes on a plant scale (1).

Boron isotope separation by using styrene–divinylbenzene strong base resin was first reported nearly 40 years ago (2). This initial report was followed by much research on separating boron isotopes by eluting adsorbed boric acid or boric acid–polyalcohol complexes from the resin with hydrochloric acid solutions (3–5).

On the other hand, efforts were made to find a cheaper eluting agent such as water and to avoid process difficulties associated with the use of strong base resins. Hirao et al. (6) found that boric acid adsorbed on weak base anion-exchange resins (also made from styrene/DVB copolymer) can be eluted by distilled water. This discovery was applied to chromatographic separation of ^{10}B by a weak base anion-exchange resin, Diaion WA-21 (7–9). The maximum enrichment (R_L) of 98.43 atom percent ^{10}B was obtained after migrating the boric acid band to a distance of 620 m (10).

Boron isotope fractionation by means of porous, 20% crosslinked resins made from 4-vinylpyridine–divinylbenzene (4-VP/DVB) was earlier reported (11). A negligible boron isotope separation was observed with the unquaternized (4-VP/DVB) resin by inverse-frontal chromatography of boric acid with hydrochloric acid solution. A good isotope separation was observed with the quaternized (4-VP/DVB) resin by inverse-frontal chromatography of boric acid–mannitol with hydrochloric acid solution.

Inverse-frontal chromatography is an operational mode of chromatography in which an ion-exchange column is first saturated with the feed solution (of the isotopes to be separated), and the loaded material is then developed with a suitable developing agent. The selectivity of the developing agent for the resin should be higher than that of all the components in the feed material to ensure "total refluxing." Inverse-frontal chromatography is suitable for the recovery and enrichment of the component which accumulates in the resin and has been applied to enrich ^{10}B which also accumulates in the resin phase (8).

Long distance inverse-frontal chromatography is necessary for the higher enrichment of ^{10}B because the separation factor of the system is close to unity. Instead of a single long column, a loop of short columns has been conveniently employed (8).

In this work, enrichment of ^{10}B by 40 m migration of boric acid–mannitol complex on a 25% crosslinked, 38% quaternized 4-VP/DVB anion-exchange resin by inverse-frontal chromatography (inverse breakthrough development) has been reported, and the overall process parameters, namely the slope coefficient (k) and the separation coefficient (ϵ), have been evaluated.

EXPERIMENTAL

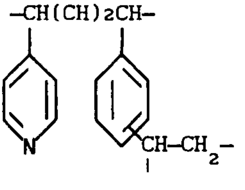
Chemicals, Resin Preparation and Characterization

All the chemicals were of analytical grade except sodium hydroxide which was of technical grade. Sodium hydroxide solution was purified by first precipitating the carbonate impurities with barium hydroxide and then filtering the solution. Distilled or deionized water was used for the preparation of the solutions.

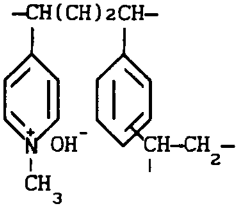
An experimental pyridine base resin was synthesized by copolymerizing 4-vinylpyridine and divinylbenzene monomers in the presence of pore-forming agents by suspension polymerization. The purity of the commercial divinylbenzene was about 60%. The crosslinkage of the polymer was 25%. The polymer beads were white in color.

The textural properties of the polymer were measured by mercury porosimetry. The measured total intrusion volume, surface area, and average pore diameter (4V/A) were 1.1437 cm^3/g, 169.805 m^2/g, and 26.9 nm, respectively. The pore size distribution of the polymer is given in Table 1.

The polymer thus obtained was quaternized with dimethyl sulfate at 60°C for 165 minutes. The total capacity of the resin (before quaternization) was measured by HCl uptake and found to be 1 $mmol/cm^3$ of the bed. Strong-base capacity of the resin was determined according to the procedure given in the literature (12) and found to be 0.38 $mmol/cm^3$ of the bed. The degree of quaternization (defined as the ratio of strong base capacity to total capacity) of the resin was about 0.38. The resin has two functional groups. The structure of these groups in free-base form is



(pyridine base 62%)



(Quaternized pyridine base in OH^- form, 38%)

Preparation of Chromatographic Columns and Operation Procedure

A loop of four Amicon glass columns, each 1 m in length and 2.2 cm in diameter with an adjustable plunger (designated as C1. . .C4 in Fig. 1),

TABLE 1
Pore Size Distribution of the Polymer

Pore size interval (nm)	3.2–5	5–10	10–50	50–100	100–200	200–500	>500
Pore volume (cm^3/g)	0.0325	0.0432	0.5221	0.2081	0.1509	0.0836	0.1033

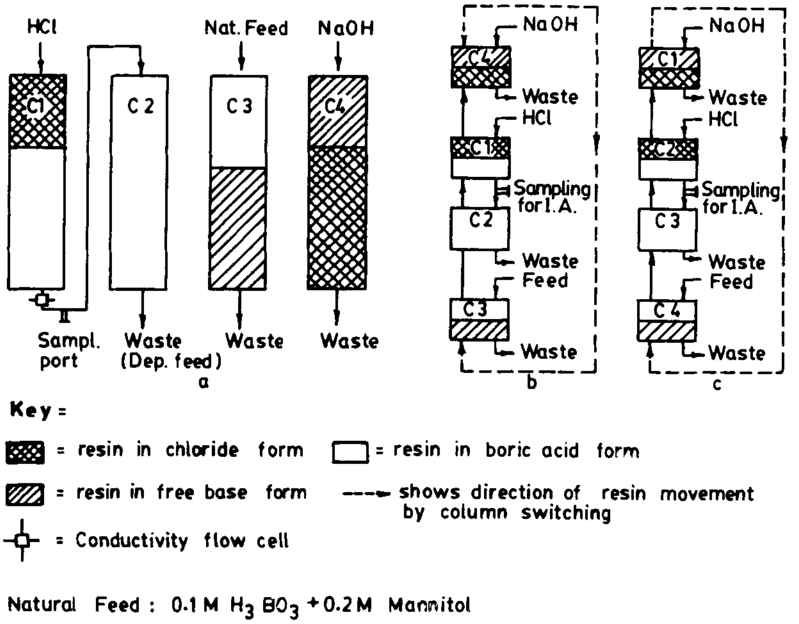


FIG. 1 (a) Column operation procedure. (b) An equivalent simulated moving-bed representation of column operation procedure (a). (c) Next switching.

was used. A resin fraction of − 125 + 45 μm (wet sieved) was packed as slurry into the columns to a desired bed height. The operational temperature was about 25°C.

Columns C1, C2, and C3 were regenerated with 1 M NaOH and thoroughly washed with deionized water. Peristaltic pumps were used for the feeding of different solutions. C1 and C2 were loaded with feed solutions containing 0.1 M H_3BO_3 (0.1985 atom% ^{10}B) and 0.2 M mannitol until saturation was reached. Effluent consisting of depleted feed was discarded. C1 and C2 were interconnected with 1 mm inside diameter tubing and C1 was connected to the developing agent (0.1 M HCl) line. At the same time, C3 was connected to the feed solution and C4 was connected to regeneration. The effluent (depleted feed) from C2 was discarded until the rear boundary was transferred from C1 to C2. This was done to keep a plateau region of the natural feed in order to avoid mixing the enriched and depleted materials. The operational procedure is shown in Fig. 1(a). For the detection of the rear boundary, the effluent from C1 was monitored with a flow-through conductivity cell (1 mL volume) connected with a conductivity meter. To monitor enrichment of ^{10}B, a few drops of sample were taken at the known effluent volume (see Fig. 1a) and isotopic analysis was determined by mass spectrometery. An equivalent representation of Fig. 1(a) as a simulated moving-bed is shown in Fig. 1(b).

After the transfer of the rear boundary from C1 to C2, C1 was isolated for regeneration and C2 was connected to C3 as well as to the developing agent line. The simulated moving-bed representation of this switching is given in Fig. 1(c). The switching was obtained by column movement.

The flow rate of the developing agent was 176 cm^3/h and the rear boundary speed was about 3 cm/h.

RESULTS AND DISCUSSION

An isotopic analysis of the band for different migration distances is given in Table 2. The data in Table 2 show that ^{10}B is enriched at the rear boundary.

TABLE 2
Isotopic Analysis of Column for Different Migration Distances

Migration distance, L_m (m)	Distance from rear boundary, d (cm)	Isotopic analysis atomic fraction, R
2.00	0	0.36
7.94	0	0.69131[a]
	−6	0.58638
	−12	0.41963
	−24	0.28730
	−36	0.22518
20.43	0	0.75380
	−1.7	0.71511
31.00	0	0.93554[a]
	−6	0.86439
	−8	0.83441
	−10	0.80086
	−20	0.53877
36.92	0	0.94620[a]
	−1	0.94150
	−4	0.91569
	−20	0.51279
	−40	0.23889

[a] Estimated values of R_L, see text.

Solution and Ion-Exchange Chemistry

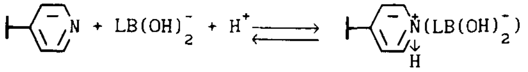
Boric acid is a very weak acid. It exists in aqueous solution mainly as an undissociated species, H_3BO_3. Therefore, boric acid does not significantly protonate the pyridine functional group of the resin. Moreover, the concentration of the anionic species, $B(OH)_4^-$, capable of anion exchange with the quaternized functional group, is also low.

The acid strength of boric acid can be increased by adding mannitol to the solution by the following overall reaction (13):

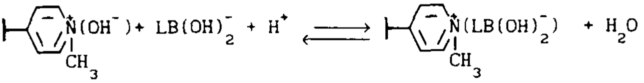
$$B(OH)_3 + LH_2 = LB(OH)_2^- + H^+ + H_2O \qquad (1)$$

where LH_2 represents mannitol and L is $HOCH_2(HCOH)_2((HC(O))_2$-CH_2OH. Equation (1) shows that the addition of mannitol to the boric acid solution increases its pH. Boric acid has a higher complex formation constant with mannitol than with other common diols like ethylene glycol, polypropylene glycol, etc. Therefore, mannitol seems to be a better reagent.

Sorption of mannitol–boric acid complex on the resin can be described by Eqs. (2a)–(2b):

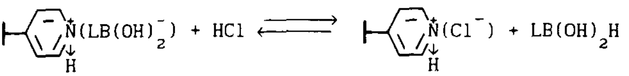


(2a)

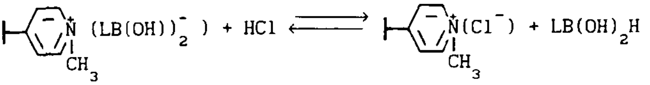


(2b)

When the boric-acid-loaded resin is developed with HCl, the following reactions take place at the rear boundary:



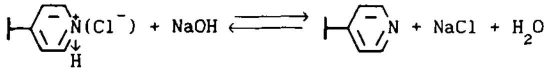
(3a)



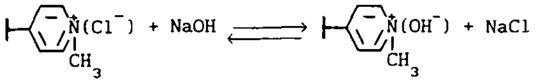
(3b)

The equilibrium constant for the above reaction is greater than 1 because the formation constant of $LB(OH)_2H$ is 4 × 10^3 (13).

Regeneration of the spent resin is done with the help of the following reactions:



(4a)



(4b)

The major isotopic exchange reaction between the resin phase and the solution phase responsible for the fractionation of boron isotopes (11) can be written as

$$\overline{\mathrm{L^{11}B(OH)_2^-}} + \mathrm{L^{10}B(OH)_2H} \rightleftarrows \overline{\mathrm{L^{10}B(OH)_2^-}} + \mathrm{L^{11}B(OH)_2H} \qquad (5)$$

where an overbar represents the resin phase. Since the equilibrium constant of the above reaction is slightly greater than 1, ^{10}B accumulates in the resin phase whereas ^{11}B accumulates in the solution phase. The addition of mannitol to boric acid solution sharpens the sorption front of boric acid on the resin (Eq. 2) and increases the isotope separation factor. Mannitol is a better reagent than glycerol for the separation of boron isotopes (14).

Data Analysis for Determination of ϵ, k, and R_L

The mathematical theory of isotope separation by ion-exchange chromatography (10) predicts that isotopic distribution within the column is given by

$$R = 1 - \frac{1 - R_0}{1 + (e^{\epsilon k R_0 L_m} - 1)e^{kd}} \qquad (6)$$

where R is the atom fraction of ^{10}B at distance d from the reference boundary to the sampling position, R_0 is the atom fraction of ^{10}B in the feed solution, L_m is the migration length and is defined as the distance traveled by the reference boundary, and k is the slope coefficient. The distance d is positive when the reference boundary is the front boundary and negative when the reference boundary is the rear one. The slope coefficient k is related to the height equivalent to a theoretical plate, H, by the following equation

$$H = \frac{\epsilon}{k}\left(1 + \frac{R_0}{e^{\epsilon k R_0 L_m} - 1}\right) \qquad (7)$$

The values of ϵ and k can either be estimated by nonlinear regression of the data (d, R) using Eq. (6) or by transforming the equation into linear form. The second approach has been followed in this paper, Equation (6) can be written in linear form as

$$\ln\left(\frac{R - R_0}{1 - R}\right) = kd + \ln(e^{\epsilon k R_0 L_m} - 1) \qquad (8)$$

with slope $(= m) = k$ and

$$y \text{ intercept } (= c) = \ln(e^{\epsilon k R_0 L_m} - 1) \qquad (9)$$

The plot of $\ln[(R - R_0)/(1 - R)]$ versus d is shown in Fig. 2. The plot is linear within experimental error, confirming the validity of Eq. (7). The values of m and c were determined by linear regression. The values of ϵ were calculated from Eq. (10), obtained by rearranging Eq. (9) as

$$\epsilon = \frac{1}{kR_0L}\ln(1 + e^c) \tag{10}$$

The estimated values of k and ϵ for different migration distances are given in Table 3. The values of k and ϵ vary with migration distance, L_m. The reason for this variation is not understood.

The maximum enrichment, R_L, can be obtained at the extreme of the rear boundary, that is, $d = 0$ and $R = R_L$. Equation (8) can be rearranged

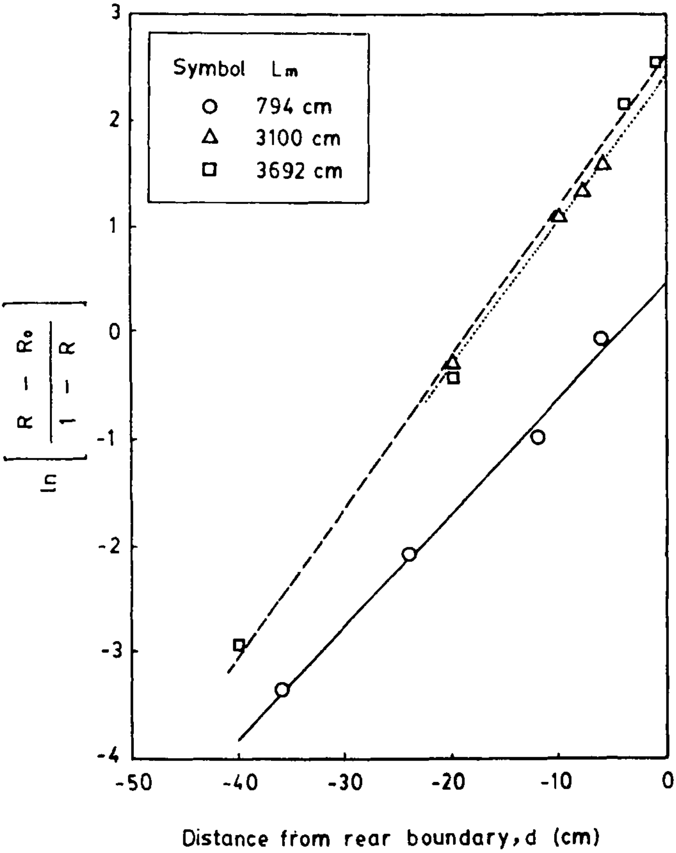


FIG. 2 Plot of $\ln[(R - R_0)/(1 - R)]$ versus distance from rear boundary, d.

TABLE 3
ϵ, k and R_L for Different Migration Distances

Migration distance, L_m (m)	0	2.00	7.94	31.00	36.92
Slope coefficient, k (cm^{-1})	—	0.1063	0.1063	0.1365	0.1419
Separation coefficient, ϵ[a]	—	—	0.056	0.03	0.0239
Maximum enrichment, R_L[b]	0.1985	0.360[c]	0.6913	0.9355	0.9463

[a] Calculated from Eq. (10).
[b] Calculated from Eq. (11).
[c] Experimental value.

to give

$$R_L = (R_0 + e^c)/(1 + e^c) \tag{11}$$

The estimated values of R_L are given in Tables 2 and 3.

Determination of Overall ϵ and k

As ϵ and k vary with L_m, an average value of these parameters is required. Since k does not vary significantly, an arithematic average of k values can be taken. The average value of k is 0.1282 cm^{-1}. An average value of ϵ can be obtained from

$$\ln[(1 - R_0)/(1 - R_L)] = (k\epsilon R_0)L_m \tag{12}$$

where R_L is the maximum atomic fraction of ^{10}B at the rear boundary. Equation (12) is obtained from Eq. (6) under the conditions $d = 0$ and $R = R_L$. Once the average value of k is known, the average value of ϵ can be determined from Eq. (12) by plotting $\ln[(1 - R_0)/(1 - R_L)]$ versus L_m. The plot is shown in Fig. 3. The value of the slope ($k\epsilon R_0$) was determined by the least-square linear regression method and found to be 7.5506×10^{-4} with a correlation coefficient of 0.997. From the value of the slope, ϵ was found to be 0.02967.

The highest value of ϵ for a styrene/DVB strong base anion exchanger with the boric acid–mannitol system has been reported as 0.027 (15), very close to the calculated value of 0.02967.

Partially quaternized 4-VP/DVB resins have another operational advantage over strong-base anion-exchange resins. The absorption of CO_3^{2-}/HCO_3^- from sodium hydroxide solution (used for regeneration from the Cl^- form to the OH^- form) on the former resin is less. This gives less evolution of CO_2 during migration of boric acid–mannitol with HCl.

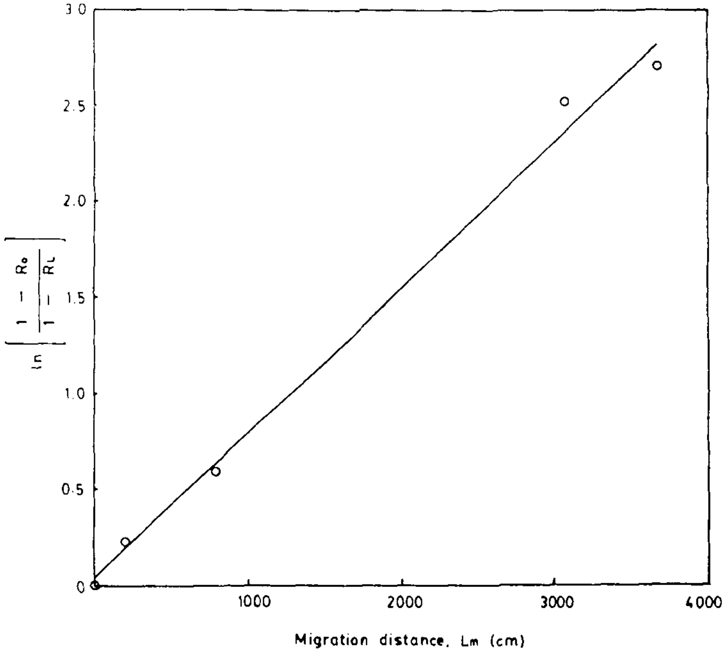


FIG. 3 Plot of $\ln[(1 - R_O)/(1 - R_L)]$ versus migration distance, L_m.

CONCLUSIONS

1. Boron isotope separation was performed by migration of the boric acid–mannitol band on a partially quaternized 4-VP/DVB resin with 0.1 M HCl. After about 40 m migration, 94.15% ^{10}B was obtained at the rear boundary.
2. The average values of the separation coefficient (k) and separation coefficient (ϵ) were found to be 0.1285 cm^{-1} and 0.03, respectively.

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