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Chromatographic Enrichment of ^{10}B by Using Weak-Base Anion-Exchange Resin

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Abstract

In order to enrich ^{10}B isotope, a boron adsorption band was eluted 620 m in a reverse-breakthrough displacement manner. Thereafter the band was stopped for 10 days and then eluted again up to a total distance of 754 m. The rear boundary of the adsorption band was kept sharp throughout the elution. From monitoring of the isotope abundance during elution, the lighter isotope ^{10}B was confirmed to be accumulated in the band end region. The maximum enrichment of ^{10}B reached 98.43% (^{10}B atomic fraction) at a migration distance of 620 m. The interruption in the operation caused no serious damage in isotope accumulation, but there was a slight broadening of the accumulation curve. The isotopic accumulation was examined based on theoretical equations previously proposed. The results indicate that the HETP of the system is constant, 1.8 mm, up to a migration distance of 620 m and increases slightly at the distance of 754 m. The separation coefficient shows a gradual decrease with an increase of migration distance: $\varepsilon = 9 \times 10^{-3}$ (at 200 m) and 7.8×10^{-3} (at 754 m).

INTRODUCTION

Boron has been used in nuclear-related fields as a neutron absorbing material. The use of boron has recently been extended to neutron capture therapy for melanotic cancer and brain tumors. Cancer tissue is destroyed in therapy by the alpha particles induced by the nuclear reaction $^{10}B(n,\alpha)^{7}Li$. To improve the efficiency of such treatments, it is important to use enriched ^{10}B.

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A ^{10}B enrichment process has been developed based on an exchange system of BF_3 and a BF_3 complex compound such as BF_3–anisole (*1, 2*). The ion-exchange process is a promising alternative for isotope separation. Yoneda et al. (*3*) first reported a study of boron isotope separation by using a strong-base anion-exchange resin. Extended studies followed (*4–10*). Hirao (*7*) found that some boron complexes adsorbed on weak-base anion exchange resin were eluted by distilled water. This was applied to chromatographic ^{10}B isotope separation by using the weak-base anion-exchange resin Diaion WA-21 (*7–10*).

Based on previous experience, the present work carries out long distance elution of the boron adsorption band in order to obtain highly enriched ^{10}B and to study the effects of chromatographic characteristics in the progression of the enrichment process.

EXPERIMENTAL

Apparatus

The experimental apparatus for the chromatographic operation consists of eight glass columns (each 3 cm i.d., 210 cm long) packed with the weak-base anion-exchange resin Diaion WA-21, 60–80 mesh (180–260 μm diameter) and equipped with a pair of platinum electrodes (1 cm diameter) for the measurement of electric conductivity in the column to monitor the band boundary. A Styrofoam floating plate was placed on the resin bed at the top part of each column to prevent the eluent from dropping directly into the bed, and an injector was stuck through the rubber stopper to adjust the solution level in the column. The temperature of the chromatography was maintained at 40°C with thermostated water circulating through the water jacket of the column. An illustration of the unit column was presented in a previous paper (*10*).

Operation

The ion-exchange resin packed in the columns was pretreated with 1 mol/dm^3 (*M*) HCl solutions to remove impurities, converted to the free base form with 0.5 *M* NaOH, and washed with distilled water. Finally, the height of the resin bed was adjusted to 200 cm by taking out any excess resin.

Then all the columns were charged with a boric acid solution, 0.1 *M* $B(OH)_3$, at a rate of 40 cm/h SV (superficial velocity) until the boric acid concentration in the effluent became 0.1 *M*. After the first loading of boric

acid was completed, the columns were divided to two groups, the eluting part and the loading part. Four columns in each group (Columns 1–4 and 5–8) were connected in series with silicon rubber tubes (0.2 cm i.d.). A peristaltic pump was mounted at each outlet of the eluting and loading parts.

The eluent, distilled water, was then admitted to Column 1 at a rate of 20 cm/h SV. At this feed rate the boric acid adsorption band was eluted at a migration rate of ~8–9 cm/h. When the band boundary passed over the platinum electrodes inserted in the bottom of the resin bed, the column connection was rearranged by turning the valves at the top and bottom of the columns. Column 1 was separated from the eluting part and connected to the loading part after Column 8. In the same way, Column 5 was connected to Column 4. These operations were continued, column by column. Thus the ion-exchange columns were operated in a merry-go-round fashion so they were cyclically subjected to loading and eluting of the boric adsorption band. The effluent from the loading part was discarded throughout the operation, since this work is concerned with isotopic accumulation at the rear boundary. The arrangement of the column connections during elution is illustrated in Fig. 1. The chromato-

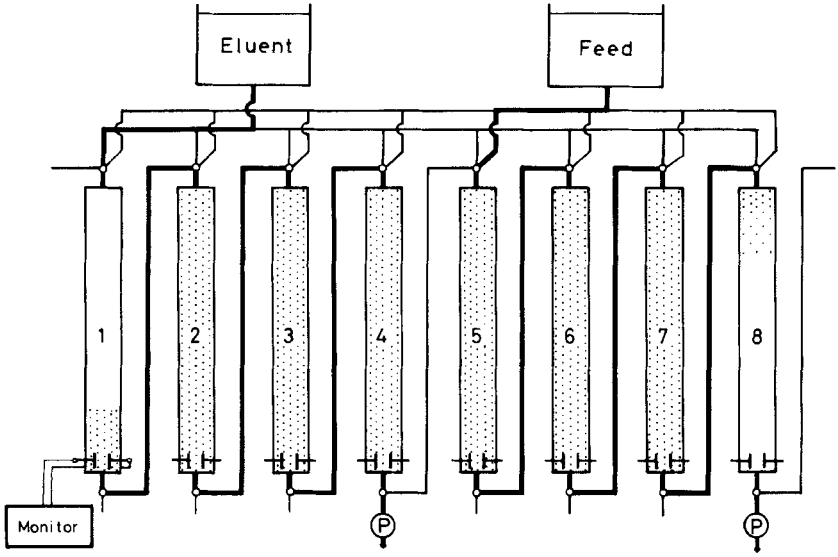

FIG. 1. Chromatographic separation system for ^{10}B enrichment. The thick lines represent the connections at a certain operation time. The dotted areas represent the boron adsorption band. The blank areas represent the free base form. Eluent: Distilled water. Feed: 0.1 *M* $B(OH)_3$. Monitor: Conductivity meter. P: Peristaltic pump.

graphic operation was continued in the first stage till the migration distance reached 620 m. After a 10-day stop due to closing of the laboratory, the operation was re-started (second stage). The total migration distance was 754 m at the end of the second stage elution.

Sampling and Analysis

When the migration distance of the band boundary approached 202, 302, 402, 502, 620, and 754 m, a few droplets of the eluent was sampled beginning 3 m before the band boundary to monitor the isotopic composition. Sampling continued at appropriate intervals of the eluent volume until the boundary moved a given distance. The abundance ratios of boron isotopes in the fractions of eluent sampled were determined with a mass spectrometer MAT CH-5 by a surface ionization method.

RESULTS AND DISCUSSION

Chemical System

Boron isotope separation using anion-exchange chromatography is based on isotope effects in the isotope-exchange reaction between the boron complex species of trigonal planar $B(OH)_3$ and tetrahedral $B(OH)_4^-$ (*8*):

$$^{10}B(OH)_3 + {}^{11}B(OH)_4^- = {}^{11}B(OH)_3 + {}^{10}B(OH)_4^- \qquad (1)$$

According to Ingri (*11*), the species of boron in aqueous solution are $B(OH)_3$ when the pH is less than 6 and $B(OH)_4^-$ when the pH is higher than 11. Between pH 6 and 11 there is a mixture of $B(OH)_3$, $B(OH)_4^-$, $(BO)_3(OH)_4^-$, and $(BO)_3(OH)_5^{2-}$. The last two species are polyborate ions, regarded as the condensation trimers of $B(OH)_3$ and $B(OH)_4^-$. Since the anion-exchange resin adsorbs the anionic species $B(OH)_4^-$ etc. and the external aqueous solution retains the boric acid molecule $B(OH)_3$, the isotope effects expressed by Eq. (1) are isotopic fractionations in the anion-exchange system.

The separation factor of single-stage ion-exchange, which is the most fundamental physicochemical property in the separation process, is defined for boron isotopes as

$$S = ([^{10}\bar{B}]/[^{11}\bar{B}])/([^{10}B]/[^{11}B]) \quad (2)$$

where [ ] denotes the isotopic concentration and an overbar indicates the resin phase. The isotope separation factor for the strong-base anion-exchange system is ~1.02–1.03 (*5, 6, 8*). On the other hand, in the case of a weak-base anion-exchange resin system, the basicity of the resin phase is low, and the major boron species in the resin are polyborate ions. As mentioned above, the polyborate ions involve the trigonal planar structure of $B(OH)_3$ and the tetrahedral structure of $B(OH)_4^-$. The existence of the trigonal planar structure species in both phases of the resin and in the aqueous solution results in a lowering of isotope effects in the weak-base resin system (*8*). The single-stage separation factor for the system has been found to be ~1.01 in previous work (*8–10*).

To carry out long-distance chromatographic elution, it is necessary to know the location of the band boundary in a column. Unfortunately, there is no visible change in the ion-exchange resin when the boric acid is adsorbed on the resin. However, the electric conductivity of the resin is increased by the adsorption of boric acid due to an increase in the abundance of the ionic species. By making use of this fact, the conductivity of the anion-exchange resin bed was measured to monitor the location of the band boundary. The technique worked satisfactorily. The monitored rear band boundary is shown in Fig. 2. The recorded shape of the boundary in the monitor is somewhat broader than the actual one due to the volume of the detected part in the ion-exchange resin bed.

During chromatographic elution it was found that the eluent volume for a unit column gradually decreases with an increase in the migration distance. This means that the ion-exchange capacity decreases over long-time, repeated use of the resin. Since the change in the resin bed height was negligibly small over approximately 50 cycles of repeated use, the capacity decrease cannot be attributed to the physical attrition of the resin but must be due to chemical decomposition of the amino functional groups in the resin. Actually, there was a smell of amines in the effluent from the columns. The capacity change is shown in Fig. 3.

Isotope Accumulation

The migration velocity of the band boundary was ~8–9 cm/h, and the migration continued for 338 days in the first-stage migration of 620 m. Results of isotope analysis of the sample fractions showed a significant enrichment of ^{10}B in the rear band boundary region. The maximum

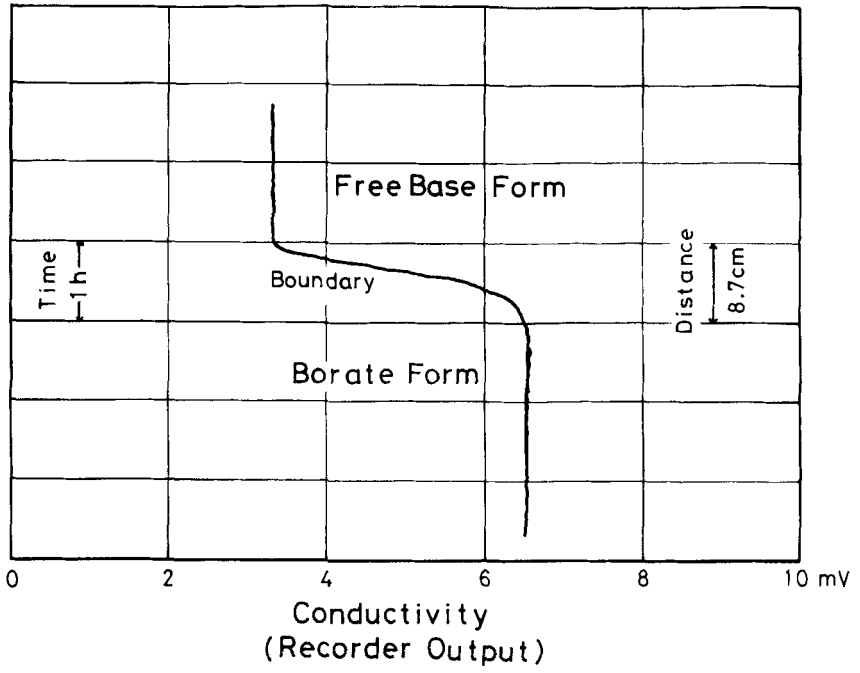

FIG. 2. The rear band end monitored by the conductivity meter.

degree of enrichment was obtained at the extreme end of the boron band for different migration distances. The maximum degree of enrichment increased with an increase in the migration distance. It reached 98.43% (^{10}B atomic fraction) at a migration distance of 620 m; the original concentration of ^{10}B in the feed boric acid was 19.84%. The observed values of the maximum degree of enrichment are presented in Table 1. The isotopic accumulation of ^{10}B in the rear region of the band continued throughout chromatographic migration, and therefore the enrichment zone expanded steadily with increase in the migration distance.

Glueckauf developed mathematical equations for isotope separation by liquid chromatography (*12*). In this theorem an equation was derived for isotopic accumulation in migrating band by displacement chromatography. Although this equation has been frequently used for studies in this field, it has been necessary to make some different approximations in the actual application of the equation to practical cases depending on the extent of the degree of enrichment of the system. Kakihana and Oi

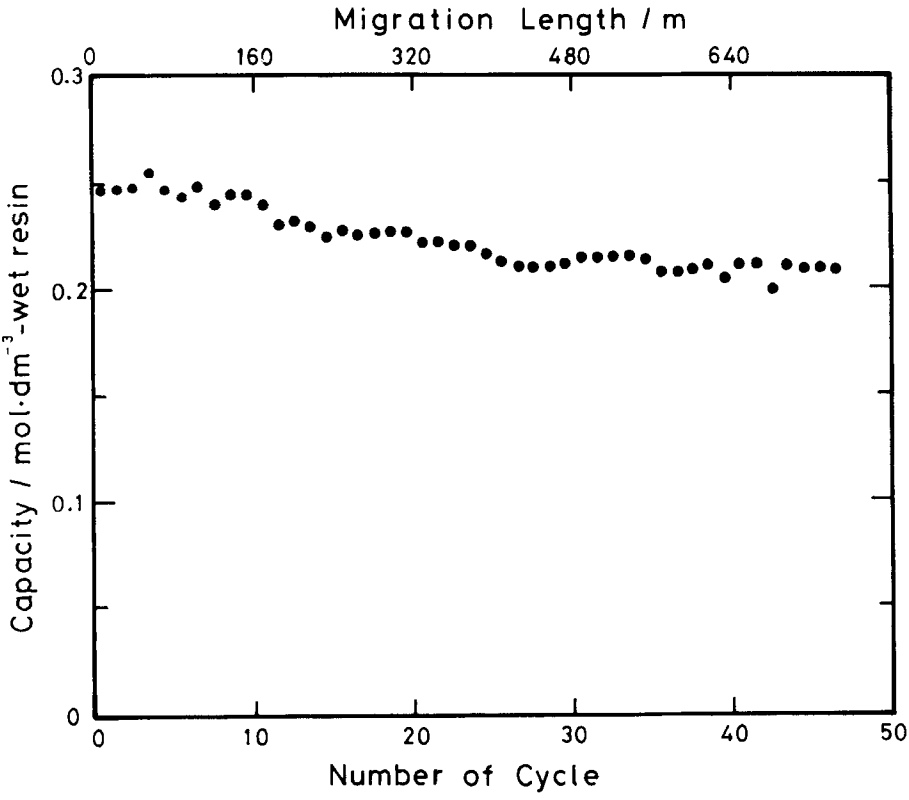

FIG. 3. The change in the ion-exchange capacity.

TABLE 1
Results of ^{10}B Enrichment by Anion-Exchange Chromatography

Migration distance (m)	Maximum enrichment of ^{10}B (%)	Separation coefficient $\times 10^3$	Slope coefficient k (cm^{-1})	HETP (mm)
202	86.11	9.0	0.051	1.77
302	93.56	8.5	0.049	1.69
402	96.55	8.6	0.047	1.84
502	97.98	8.3	0.045	1.74
620	98.43	8.1	0.041	1.86
754	98.31	7.8	0.035	2.04

developed another type of theorem for displacement chromatography isotope separation (*13*); the set of equations from this theorem is applicable to a system with low enrichment.

In a previous paper (*14*) we proposed more convenient equations to analyze chromatographic data on isotope separation. The results are summarized as follows:

$$\ln (r - r_0) = k(x - L) + \ln g, \qquad g = r_L - r_0 \tag{3}$$

$$R = 1 - (1 - R_0)/[1 + (e^{\varepsilon k R_0 L} - 1)e^{k(x-L)}] \tag{4}$$

$$\varepsilon = (kR_0L)^{-1} \ln [(R - R_0)(1 - R)^{-1}e^{-k(x-L)} + 1] \tag{5}$$

$$H = \varepsilon r_L/k(r_L - r_0)$$

$$= \varepsilon[1 + R_0/(e^{\varepsilon k R_0 L} - 1)]/k \tag{6}$$

$$r = R/(1 - R) \tag{7}$$

where r is the isotopic ratio (here $r = [^{10}B]/[^{11}B]$), R is the atomic fraction (of ^{10}B), k is the slope coefficient, L is the migration distance, x is the distance from the starting point, ε is the separation coefficient ($\varepsilon = S - 1$), H is the HETP, and subscripts 0 and L indicate the feed material and the location of the boundary, respectively. The slope coefficient of the isotopic accumulation curve is determined by plots of the experimentally measured isotope ratios following Eq. (3). The integral of Eq. (3) leads to Eq. (4), which expresses the S-shaped function for the profile of isotope accumulation in the atomic fraction. Equation (4) is rearranged to Eq. (5), which gives the value of ε by the substitution of a set of data for one measured point (R, x). The value of the height equivalent to the theoretical plate (HETP), H, is obtained by using Eq. (6).

The experimentally determined isotopic ratios for the sample fractions in the band are presented in Fig. 4 where the isotopic abundance ratios $^{10}B/^{11}B$ are plotted against the internal distance from the band boundary. The plots fall on the straight lines for each case of different migration distances. This confirms the constancy of the slope coefficient in the band at a given migration distance or time. The determined values of k as the slopes of the lines in Fig. 4 are listed in Table 1.

The separation coefficients, ε, for different migration distances were calculated using the experimental data and Eq. (5). The calculated values of ε are listed in Table 1, which shows that the values of ε slightly decrease with an increase in the migration distance. As previously mentioned, the isotope effect or the separation coefficient depends on the basicity of the

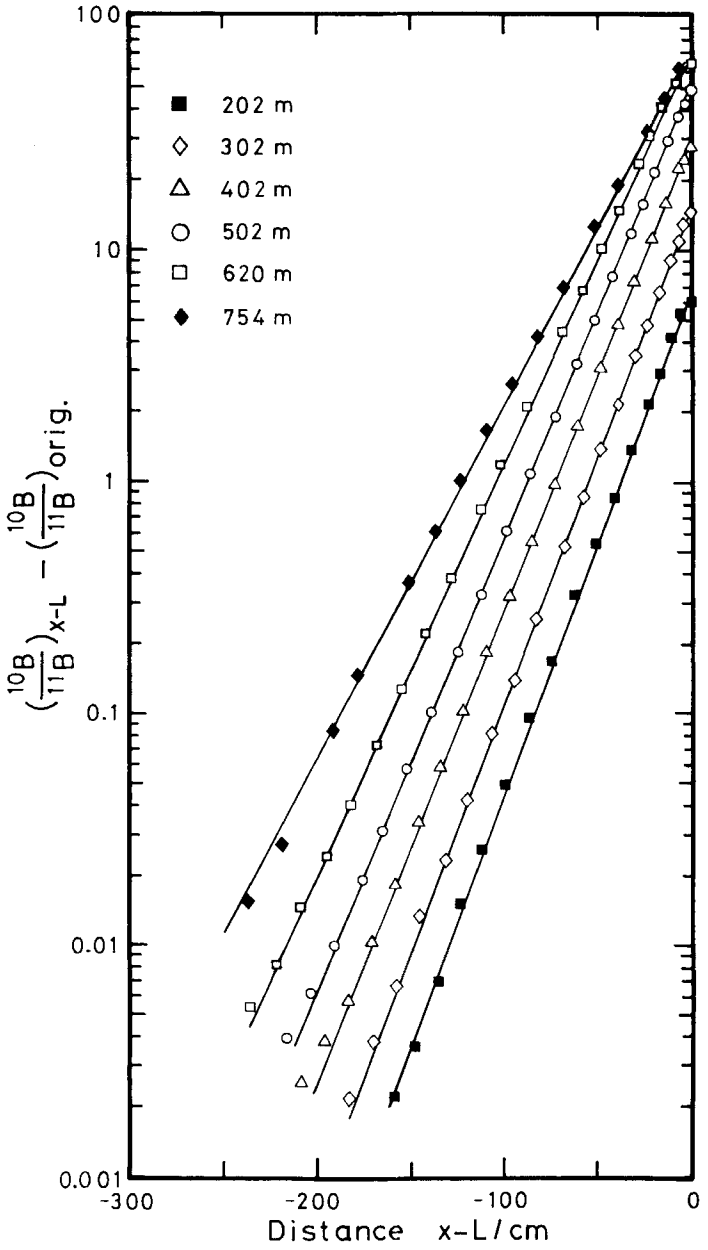

FIG. 4. Plots of the measured isotopic ratios at different migration distances vs the inner band distance. The k's indicated are the slopes of the lines in cm^{-1}.

anion-exchange resin. It is easily deduced that the decrease in the number of the fixed amino groups in the resin lowers the basicity of the resin phase, which results in a decrease of the separation coefficient.

Using the determined values of ε, k, and the experimental conditions of L and R_0, the isotope accumulation curves were calculated by Eq. (4) and drawn in Fig. 5 where the isotopic composition is indicated with the atomic fraction of the ^{10}B isotope. The corresponding experimentally observed values are plotted in this figure as well. The experimental data agree well with the calculated curves.

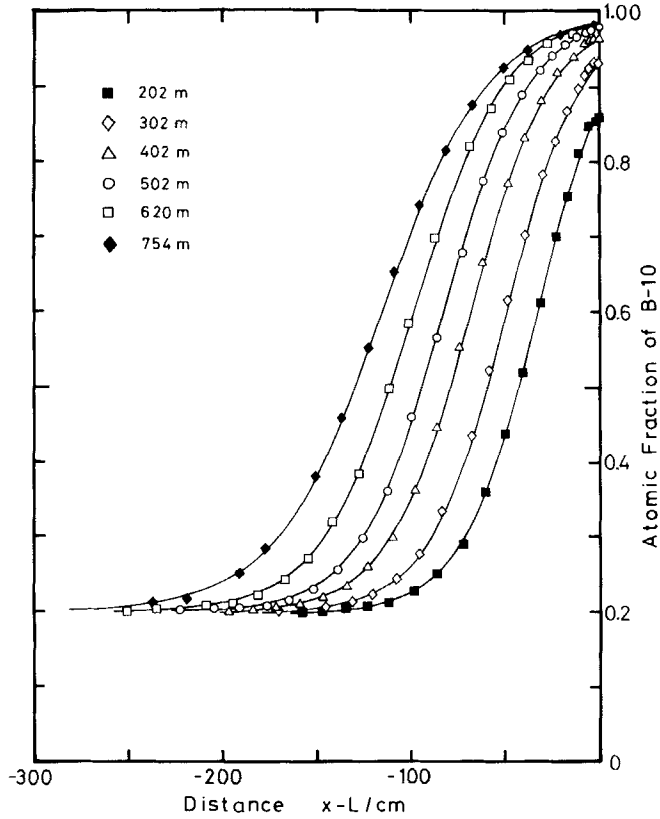

FIG. 5. The isotopic accumulation profiles at different migration distances. The solid curves were calculated with Eq. (4).

HETP

As mentioned in the preceding section, HETP was determined from Eq. (6) by using the observed values of ε and k and the experimental conditions of R_0 and L; r_L and r_0 can be used instead of L and R_0. The determined values of H for different migration distances are listed in Table 1 and are plotted in Fig. 6 along with the values of k.

In Fig. 6 it is seen that H is almost constant, 1.8 mm, over the range of migration distance up to 620 m, while H for 754 m is slightly larger, 2.0 mm. This is probably due to the previously mentioned fact that chromatographic operation was stopped for 10 days. Although the operational interruption did not cause serious damage to the accumulated isotope distribution, it did result in slight diffusion of the isotopes in the boron band. Due to this diffusion, maximum enrichment at the end

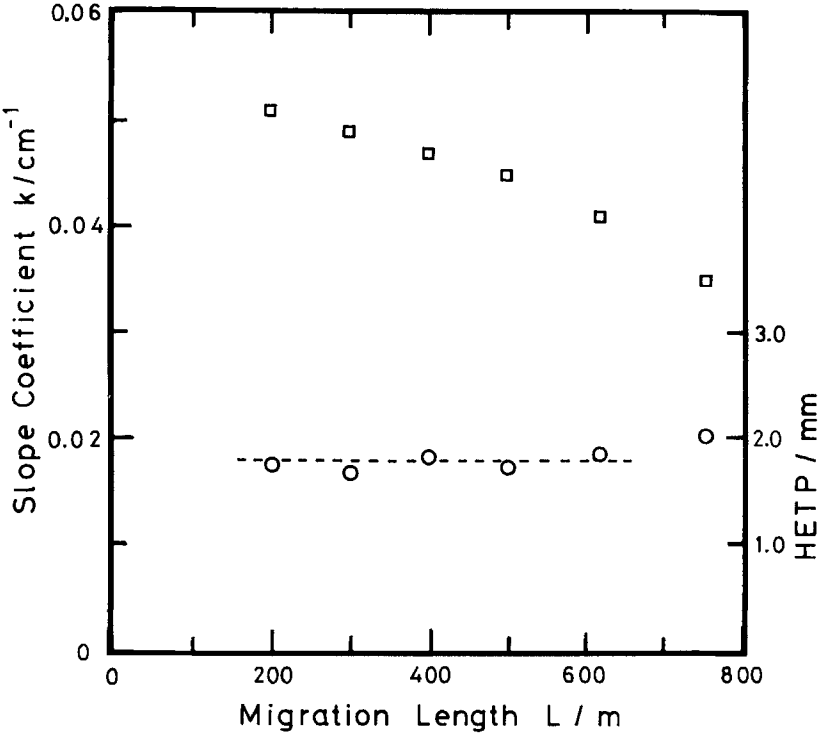

FIG. 6. The observed slope coefficients and HETP's of the chromatographic enrichment system. The dashed line shows the average value of 1.8 mm for HETP.

did not exceed the earlier maximum of 98.43%. This behavior of isotopic diffusion results in expansion of the enrichment zone and reduction of the slope coefficients. In previous work (*14*) the presently examined equations were first applied to the reported experimental data (*9*) on ^{10}B separation by using the same chemical system operating under similar experimental conditions. In that work the value of H for the chromatographic system was calculated to be 1.8 mm over a migration range up to 128 m. This value of H coincides with the one obtained in the present work.

CONCLUSIONS

Long-distance (total of 754 m) displacement chromatography of the boric acid adsorption band was successfully conducted, and a maximum enrichment of 98.43% ^{10}B was obtained at a migration distance of 620 m.

By applying the previously derived theoretical equations, the separation coefficients ε, the slope coefficients k, and the HETP H were calculated for the chromatographic separation system at different migration distances. The values of ε and k were found to decrease gradually in the course of long-distance migration, while the values of H were constant up to 620 m.

Ion-exchange capacity was found to decrease gradually. This was suggested to be responsible for the decrease of the separation coefficient.

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