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A Theoretical Study of Isotope Separation by Displacement Chromatography

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Abstract

A set of equations is derived to describe mathematically the isotope distribution in the separation process of displacement chromatography. Emphasis is placed on nonsteady-state isotope accumulation in the boundary region of a migration band. The results indicate that the isotope profile in the migration band is expressed by

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

where R, ε, k, R_0, L, and x are local isotope fraction, separation coefficient, slope coefficient, original isotope fraction, migration length, and position in the band, respectively. Mathematical treatment is extended to the determination of HETP of experimental systems. The relation between the frontal isotope ratio r_L and the migration length is also obtained. The validity of the derived equations is verified by using the reported experimental data on boron isotope separation by ion-exchange chromatography.

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INTRODUCTION

Isotope separation by ion-exchange chromatography has been extensively studied while seeking its practical application to the production of enriched isotopes. The remarkable success in ^{15}N isotope enrichment by this method was described by Spedding (*1*). Regarding the mechanism of the enrichment process, Glueckauf developed a theory for chromatographic isotope separation based on two-phase equilibrium (*2, 3*). Kakihana derived equations for isotope separation by displacement chromatography based on the concept of individual isotopic mass flows in a generalized homogeneous medium (*4, 5*). A numerical method was reported by Fujine (*6*) and Calusaru (*8*), and analytical work was done by Jacques on displacement enrichment (*7*).

Most of the above-mentioned work has been successfully applied to low-enrichment isotope separation systems; however there has been ambiguity and inconvenience in the application of the theories to highly enriched systems. The only empirical equation for highly enriched systems was obtained by Glueckauf (*3*) and applied to ^{15}N isotope separation reported by Spedding. There are specific difficulties in the general treatment of the nonsteady-state isotope separation process when it is continuously developing from low degrees to high degrees of enrichment. In the present paper the authors derive a convenient equation applicable to the nonsteady-state enrichment process covering a wide range of enrichment degrees. The equations derived are useful in estimating the feasibility of the enrichment systems experimentally considered.

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THEORY

Displacement chromatography is an efficient process for obtaining enriched isotopes. This operation is characterized by sharp band boundaries at the migration band ends. In the present work we mainly deal with displacement operating in a breakthrough manner where the sharp boundary is at the front end.

In a chromatographic separation system, one isotope species, e.g., isotope A, moves forward faster than does the other isotope. To formulate the separation process, treatment usually commences with setting up a fundamental diffusion equation for one of the species and then solving the equation under the appropriate conditions. This mathematical treatment is pertinent when isotopes A and B behave as independent species. In the case of displacement chromatography, species A and B interfere with each other: an increase in the concentration of A is always

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coupled with a decrease in the concentration of B, since the total concentration is strictly fixed in the migration band. To express such a coupled movement it is relevant to consider the relative movement of the species involved rather than the independent movement of the species. This consideration corresponds to chemical treatment in which one of the isotopes is chosen as the reference material, in contrast to the usual pattern of using the medium as the reference.

Fundamental Equation

The total concentration of isotopes in a migration band is a constant, C_0,

$$C_A + C_B = C_0 \qquad (0 \leqslant x \leqslant L) \tag{1}$$

$$C_A = C_0 R, \qquad C_B = C_0(1 - R)$$

where subscripts A and B denote the isotopes, and R is isotope fraction of A. Equation (1) is used for breakthrough migration. This relation is applicable within the limited width of the band in the case of fixed band migration. Using the terms in Eq. (1), the isotope ratio is defined as

$$r = C_A/C_B = R/(1 - R) \tag{2}$$

The isotope enrichment process in the migration band is interpreted in such a way that (a) the enrichment flow originates from the inherent isotope effect involved in the system, (b) part of the enrichment flow is canceled by a diffusion flow induced by the gradient of isotopic concentration, (c) the enrichment flow is partly consumed in increasing the concentration of the isotope of concern (namely the holdup), and (d) the rest of the enrichment flow forward through the migration band as a potential product flow.

To consider each microscopic flow component, we set up equations based on the relative flow difference between isotopes A and B. The flux of each isotopic flow is expressed by

$$\phi_A = C_A V_A, \qquad \phi_B = C_B V_B \tag{3}$$

where V_A and V_B are the overall migration velocities of isotopes A and B. Based on the concept of isotope effect in the process, the enrichment flow is written as

$$\Delta\phi_E = C_A(V_A - V_B) \tag{4}$$

Since the isotope effect in the system is defined as

$$\varepsilon = (V_A - V_B)/V_B$$

the enrichment flow is expressed as

$$\Delta\phi_E = \varepsilon C_A V_B \tag{5}$$

where ε is the separation coefficient of the system.

The relative diffusion flow is usually given in the form

$$\Delta\phi_D = -(D_A dC_A/dx - D_B dC_B/dx)$$

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where D_A and D_B are the self-diffusion coefficients of the given isotopes. This equation is applicable when each flow moves independently. In the case where the total concentration is constant, the difference in the diffusion flows of isotopes induces a compensating flow that cancels the imbalance in the diffusion flow. To avoid this complexity, we obtained a more strictly applicable equation to express the relative diffusion flow (Appendix I):

$$\Delta\phi_D = -DC_B d(C_A/C_B)/dx \tag{6}$$

The relative holdup flow used to change the isotope concentration in the narrow region Δx at position x is given by

$$\Delta\phi_h = -\Delta x(dC_A/dt - dC_B/dt) = -2\Delta x dC_A/dt$$

Thus we obtain the production flow as

$$\begin{aligned}\Delta\phi_P &= \Delta\phi_E + \Delta\phi_D + \Delta\phi_h \\ &= \varepsilon C_A V_B - DC_B d(C_A/C_B)/dx - 2\Delta x dC_A/dt \end{aligned} \tag{7}$$

To simplify the mathematical expression, we introduce a dimensionless equation obtained by dividing Eq. (7) by the flux of isotope B, ϕ_B,

$$J_P = \Delta\phi_P/\phi_B, \qquad J_E = \Delta\phi_E/\phi_B, \qquad J_D = \Delta\phi_D/\phi_B, \qquad J_h = \Delta\phi_h/\phi_B$$

$$\begin{aligned} J_P &= J_E + J_D + J_h \\ &= \varepsilon r - D dr/dx - 2(\Delta x/C_{\mathrm{B}}V_{\mathrm{B}}) dC_{\mathrm{A}}/dt \end{aligned} \tag{8}$$

Equation (8) is the fundamental equation. To apply it to the actual separation systems, we consider three typical cases of the operational state.

1. Steady State. In this state the separation process proceeds without concentration changes in the system. Moreover, no production is obtained since the production flow is totally canceled by macroscopic diffusion between the enriched part and the depleted part in the separation system. Therefore, this state is expressed by $J_P = J_h = 0$. This leads to

$$J_E + J_D = 0 \tag{9}$$

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2. Quasi-Steady State/Dynamic Steady State. The dynamic steady state corresponds to the nomal mode of operation of chemical separation plants. The plants are operated under the condition of constant productivity and no holdup change; that is, J_P = constant and $J_h = 0$. When this mathematical model is applied to a microscopic or momental mass balance in a kinetic process, this state usually refers to a quasi-steady state. The fundamental equation for the quasi-steady state or the dynamic steady state is accordingly given by

$$J_E + J_D = \text{constant} \tag{10}$$

3. Nonsteady State. In general, nonsteady-state displacement enrichment refers to the separation process operated under the total reflux condition with no production; namely, $J_P = 0$. We obtain the general relation for this state as

$$J_E + J_D + J_h = 0 \tag{11}$$

Equation (11) is a partial differential equation. It is extremely difficult to solve the equation for general conditions. Only in limited cases of, for example, low degrees of enrichment is Eq. (11) solved with some approximations. In such cases, Eq. (11) is expressed in terms of isotope fraction *R*, and becomes of the same type as the equation previously studied (*3*, *4*).

Isotopic Concentration Functions

Steady-state isotope enrichment is attained by long distance migration with a narrow band. The mathematical treatments for this state have been well studied (*1, 9–12*). In the present paper a brief description is made of this process to compare it with nonsteady state enrichment. The fundamental equation for this state is given by Eq. (9), which is written as

$$\varepsilon r - (D/V)dr/dx = 0 \tag{9'}$$

By integrating Eq. (9′) under the condition $r = r_0$ at $x = x_0$, with the terms ε, D, and V constant, we obtain the isotopic concentration function for steady-state enrichment as

$$r = r_0 e^{k_s(x - x_0)}, \qquad k_s = \varepsilon V/D \tag{12}$$

where k_s refers to the slope coefficient of the steady state, r_0 is the original isotope ratio, and x_0 is the position in the band where the isotope ratio is equal to r_0.

The nonsteady-state enrichment process, on the other hand, is described in principle by Eq. (11). Due to the previously mentioned difficulties in obtaining a general solution of Eq. (11), we propose the concept of stepwise enrichment in migration. The migration band moves forward, building a new frontal microsegment. During the short period of the stepwise formation of a new segment, the isotopic concentration in the migration band is assumed to remain intact and the product flow discharged from the front band deposits in the new segment. This process is regarded as the momental or quasi-steady state, which suggests that Eq. (10) is applicable to this system in place of Eq. (11). On the basis of the above assumption, we obtain the equation for the nonsteady-state enrichment by solving Eq. (10) under the conditions $r = r_0$ and $dr/dx = 0$ at $x = 0$, with ε, D, and V constant:

$$\varepsilon r - (D/V)dr/dx = \varepsilon r_0 \tag{13}$$

Furthermore, it is of interest to examine the state of the extreme front segment where the product flow deposits are converted to the holdup flow. This state is expressed by

$$J_p = J_h \tag{14}$$

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Combination of Eqs. (8) and (14) leads to

$$J_E + J_D = 0$$

This equation is the same as one previously obtained for the steady state, Eq. (9). This means that the steady-state model is applicable to the extreme front segment in the nonsteady state.

Using the same conditions as for Eq. (13), and paying attention to the region near the front band end whose position is indicated by the migration length L, we obtain the isotopic concentration function as

$$r - r_0 = ge^{k(x-L)} \tag{13'}$$

$$k = \varepsilon V/D, \qquad g = r_L - r_0$$

where k is the slope coefficient of the function for nonsteady-state enrichment and r_L is the isotope ratio at the front end. It should be noted that the value of exp $(-kL)$, obtained by substituting $x = 0$ in Eq. (13′), is approximated to be zero, since isotope enrichment is observed after sufficiently long migrations. Equation (13′) clearly indicates that plotting of ln $(r - r_0)$ against $(x - L)$ for experimental data yields a linear line with a slope of k despite the migration length or the extent of enrichment.

To visualize the profile of isotope accumulation at the front band region, it is necessary to express the term g by other operational factors. For this purpose Eq. (13′) is rearranged using the term for isotope fraction R in place of isotope ratio r:

$$R - R_0 = (1 - R_0)^2ge^{k(x-L)}/\{(1 + (1 - R_0)ge^{k(x-L)}\} \tag{15}$$

As presented in Appendix II, the integral of Eq. (15) between $x = 0$ and L leads to

$$g = (e^{\varepsilon kR_0L} - 1)/(1 - R_0) \tag{16}$$

Hence, we obtain the isotope profile for the enrichment at the nonsteady-state as

$$R = 1 - (1 - R_0)/\{1 + (e^{\varepsilon kR_0L} - 1)e^{k(x-L)}\} \tag{17}$$

Equation (17) is part of an S-shaped function in the range $R_0 < R < 1$: a complete S-shape is obtained when $L = \infty$. This function has a symmetric center at the deflection point $R = (1 + R_0)/2$.

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In the early stage of enrichment, where R deviates slightly from R_0 (namely, $\varepsilon k R_0 L \ll 1$), Eq. (17) is simplified to

$$R = R_0 + \varepsilon k L R_0 (1 - R_0) e^{k(x - L)} \tag{18}$$

Equation (18) is exactly the same as the one previously derived for a low enrichment system (*13*), based on the theory presented by Kakihana et al. (*4*).

HETP

The height equivalent to the theoretical plate, HETP, of chromatographic separation systems is denoted by H and defined as

$$H dr/dx = \varepsilon r \tag{19}$$

Equation (19) is rearranged to

$$d \ln r/dx = \varepsilon/H \tag{19'}$$

The HETP defined by Eq. (19) is an indicator of the steepness of the isotopic concentration function as expressed in terms of ln r.

At the steady-state enrichment, HETP is easily related to the slope coefficient. The combination of Eqs. (12) and (19) leads to

$$H = D/V = \varepsilon/k_s \tag{20}$$

The value of HETP or the slope of ln r is constant over the entire region of the migration band.

In the case of nonsteady-state enrichment, the slope of ln r increases with an increase of x and reaches a maximum value at the band front $x = L$. The maximum slope at the band front is specific to the given separation system and is expected to be kept constant through the entire process from low enrichment to high enrichment under the nonsteady state. As mentioned in the preceding section, the steady-state model $J_E + J_D = 0$ holds in the extreme front segment of the nonsteady-state enrichment system. Thus we obtain

$$[d \ln r/dx]_{x = L} = \varepsilon/H = k_s \tag{21}$$

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From Eq. (13′), $[d \ln r/dx]_{x=L} = k(r_L - r_0)/r_L$, and by the combination of this relation and Eq. (21), the slope coefficient is given as

$$k = \varepsilon r_L/H(r_L - r_0) = k_s r_L/(r_L - r_0) \tag{22}$$

Substitution of Eq. (16) into Eq. (22) leads to

$$H = \varepsilon r_L/k(r_L - r_0) = \{1 + R_0/(e^{\varepsilon k R_0 L} - 1)\}\varepsilon/k \tag{23}$$

When the enrichment degree is low (namely, $\varepsilon k R_0 L \ll 1$), Eq. (23) is simplified to

$$H = (\varepsilon/k) + (1/k^2 L) \tag{24}$$

In the case of a highly enriched system, the curve of ln r in the nonsteady state approaches the asymptote of the line for the steady-state enrichment. This fact is explained by the relation

$$d \ln r/dx = k(r - r_0)/r = k_s(r - r_0)r_L/r(r_L - r_0) \tag{25}$$

Within the region where $r_L \geqslant r \gg r_0$, the slope of ln r can be approximated by k_s.

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Estimation of Required Migration Length and Enrichment Width

To examine the feasibility of a certain chromatographic enrichment system, one has to know the migration length required to obtain the desired degree of enrichment. The relation between the maximum enrichment degree at the band front and the migration length is given from Eq. (17) by

$$R_L = 1 - (1 - R_0)/e^{\varepsilon k R_0 L}$$

or

$$L = (1/\varepsilon k R_0) \ln \{(1 - R_0)/(1 - R_L)\} \tag{26}$$

The migration length is also expressed by using HETP instead of the slope coefficient k. The combination of Eqs. (22) and (26) leads to

$$L = \frac{H(R_L - R_0)}{\varepsilon^2 R_0(1 - R_0)R_L} \ln \frac{1 - R_0}{1 - R_L} = \frac{H(r_L - r_0)(1 + r_0)}{\varepsilon^2 r_0 r_L} \ln \frac{1 + r_L}{1 + r_0} \tag{27}$$

The plant equilibrium time t (the time required to reach the production stage from start-up) is simply given by

$$t = L/V \tag{28}$$

In the present derivation we assume that isotopic composition takes its original value at the starting point $x = 0$, and differs from the original in all other places in the migration band. For most of the migration band, however, isotope composition practically appears as a plateau with an isotope ratio of approximately r_0. If we define the enriched part as the area where the isotope ratio is higher than the original value by at least a factor of ε, then the width of the enriched part for the nonsteady-state system, W, is obtained by substituting the relations $x - L = -W$ and $r = (1 + \varepsilon)r_0$ in Eq. (13′) and using Eqs. (16), (22), and (26):

$$W = H(r_L - r_0)(\varepsilon r_L)^{-1} \ln (r_L - r_0)/(\varepsilon r_0) \tag{29}$$

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APPLICATION

In order to examine the validity of the equation derived in the present work, the experimental data reported were analyzed by using the derived equations.

Sakuma et al. studied the enrichment of ^{10}B isotope by anion-exchange chromatography carried out in a reverse breakthrough operation (*14*). In this work, natural boron in the form of boric acid was fed into separation columns packed with weakly basic anion-exchange resin, and then the adsorbed boron was eluted by displacement by pure water, forming a sharp boundary at the rear end. By recyclic use of packed columns (1 m long) connected in series, chromatographic migrations were performed up to 256 m. After migration the effluents were subjected to mass-spectrometry analysis, and the isotope ratios of ^{10}B and ^{11}B were determined.

To apply the equations derived in the present paper, the isotope profile in the effluent was converted to the isotope profile in the migration band in the column at migration length L. Figure 1 shows plots of the isotope ratio ln $(r - r_0)$ against the distance $(x - L)$ in the ion-exchange column.

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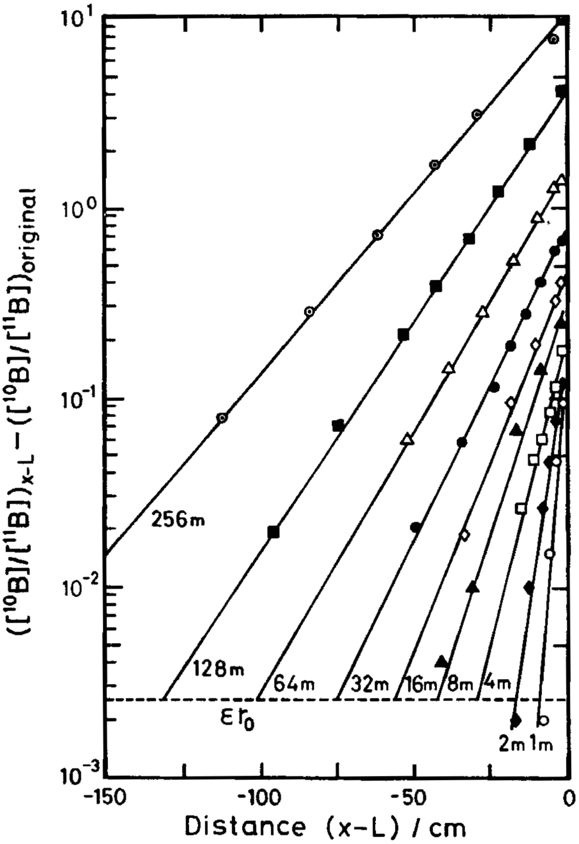

FIG. 1. The relation between the isotope enrichment degree ln $(r - r_0)$ and the distance from the band end $(x - L)$. System: Boron isotope separation by displacement anion-exchange chromatography (experimental data are from Ref. *14*). Migration length: 1-256 m as indicated for each run. Original isotope ratio r_0 = 0.2475.

The linearity of the plots for each run indicates both the validity of Eq. (13′) and the constancy of the slope coefficient k over the entire enriched zone region. It was also found that the value of k depends on the migration length. By using Eq. (23), the values of HETP for different migration lengths were calculated. They are presented in Fig. 2 along with the values of k determined by using the plots in Fig. 1. Figure 2 clearly shows that the HETP of different migration lengths is constant over a wide range of migration lengths (from 2 to 128 m). Deviations in HETP values were found in the extreme cases, i.e., migration lengths of 1

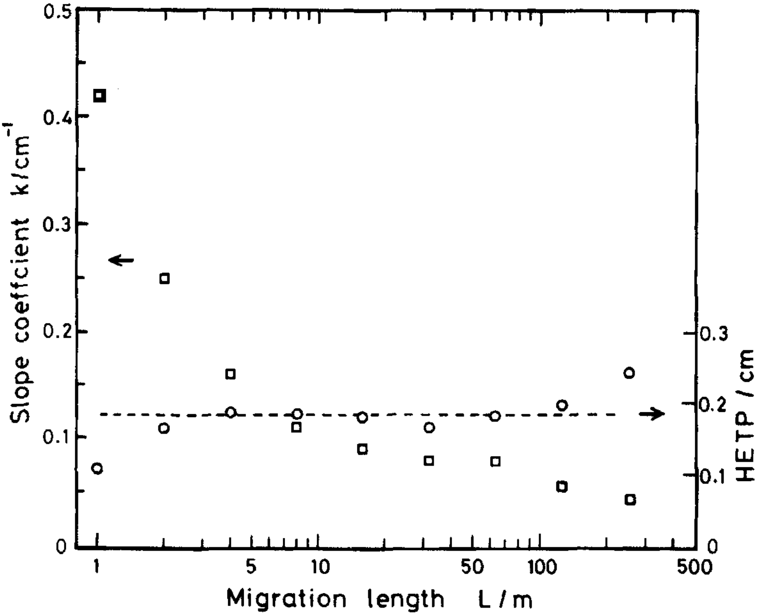

FIG. 2. HETP's and slope coefficients (k) of the boron isotope separation by displacement anion-exchange chromatography. (□) k determined by the plotting in Fig. 1. (○) HETP calculated by HETP = $\varepsilon r_L/k(r_L - r_0)$, $\varepsilon = 0.01$, $r_0 = 0.2475$, r_L = experimental isotope ratio at band end, from Ref. *14*. The dashed line is the average of the HETP's, 0.18 cm.

and 256 m. In the case of 1 m migration, chromatography was carried out by using a single column only without any connecting columns. Presumably, this is the prime reason for the small HETP value. On the other hand, in the case of 256 m migration, there was an interruption in the operation due to mechanical trouble in the apparatus (*15*). This may be the reason for the large HETP value at 256 m. This process of anion-exchange chromatography has the advantage of operational stability for mechanical troubles. When trouble happens, the supply of eluent and the circulation of thermostated water are stopped immediately. Then the column temperature decreases, which causes adsorption of the exchange resin for the boron ions in the solution phase. Thus, isotope remixing is lowered. When the trouble is eliminated, the temperature is elevated to the operational level and normal conditions are reestablished for chromatographic migration.

By using the same experimental study for boron isotope separation, the validity of Eqs. (26) and (29) was examined. Figure 3 depicts (a) the relation between maximum enrichment at the band end and the

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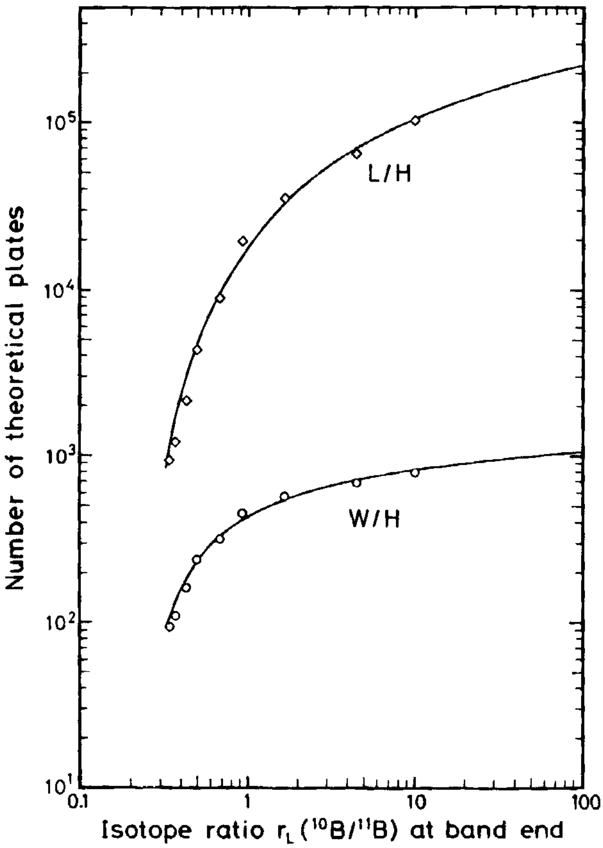

FIG. 3. Migration length and enrichment width in the number of theoretical plates vs isotope ratio at the band end. Solid curves are calculated for the boron isotope separation system with $\varepsilon = 0.01$, $r_0 = 0.2475$. Experimental data cited from Ref. *14*. (◇) Migration length *L*/HETP, (○) enrichment width *W*/HETP. *W*'s were determined by the plots in Fig. 1. HETP's used are shown in Fig. 2.

migration length expressed in terms of the stage number (*L*/*H*), and (b) the relation between the width of the enriched part in *W*/*H* and maximum enrichment at the band end. The curves were drawn by using the specific values of the experimental system, $\varepsilon = 0.01$ and $R_0 = 0.1984$. The plots in Fig. 3 are experimentally observed values. It is seen that the experimental values are in good agreement with the calculated ones.

In the present analysis procedure for chromatographic isotope separation, if R_0, H, and R_L are given, the required length of migration L and the slope coefficient k are readily calculated by using Eqs. (22) and (27).

In the similar case where L is given but R_L is unknown, it is necessary to calculate R_L by a graphical method or by a computer method employing Eq. (27). Figure 3 is a typical example where R_L is read against a given value of L/H.

CONCLUSION

A fundamental equation for flow balance in isotope separation by chromatography was formulated based on the concept of relative movement of isotopes in the enrichment and diffusion processes.

By introducing the quasi-steady-state model of constant production flow, the fundamental equation was solved for nonsteady-state isotope accumulation at the front boundary region of a displacement migration. The equation derived can cover a wide range of degrees of isotope enrichment.

The mathematical treatments were extended to find the relations between the slope coefficient k and HETP, between the migration length L and the maximum enrichment degree R_L, and between R_L and the width of the enriched part W.

The validity of the derivation was ascertained by the application of the derived equations to experimental data reported for boron isotope separation by displacement anion-exchange chromatography. The HETP of the experimental system examined was calculated to be 0.18 cm.

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APPENDIX

I. To consider the diffusion of enriched isotopes, we introduce the concept of relative diffusion between isotopes A and B. In the same way as in the derivation of Fick's law in the thermodynamics of irreversible processes, we start with the chemical potentials of isotopes:

$$\mu_A = \mu_A^0 + R^*T \ln C_A, \qquad \mu_B = \mu_B^0 + R^*T \ln C_B \tag{A-1}$$

where R^* is the gas constant and T is the absolute temperature. Taking B as the reference state material, the chemical potential of A to B is given as

$$\mu_{A/B} = \mu_A^0 - \mu_B^0 + R^*T \ln C_A/C_B \tag{A-2}$$

The driving force of diffusion for this process is expressed as

$$F = -d\mu/dx \tag{A-3}$$

and the flux of diffusion, ϕ_D, is expressed as

$$\phi_D = \omega C_A F \tag{A-4}$$

where ω is the mobility of the given species.

Since the product of ω, R^*, and T is equal to the diffusion coefficient of this process, D, we obtain the following diffusion flux:

$$\phi_D = -DC_B d(C_A/C_B)/dx \tag{A-5}$$

II. Equation (15) is integrated between the starting point $x = 0$ and the migration front end $x = L$.

$$\int_0^L (R - R_0)dx = \frac{(1 - R_0)}{k}(\ln \{1 + (1 - R_0)g\} - \ln \{1 - (1 - R_0)ge^{-kL}\}) \tag{A-6}$$

Equation (9) indicates that the term ge^{-kL} on the right-hand side of Eq. (A-6) is practically zero at $x = 0$. Regarding the integral of the left-hand side, we can make use of the well-known equation used to determine the single-stage separation factor S, or separation coefficient ε, first derived by Spedding et al. (*1*):

$$\varepsilon = S - 1 = \Sigma\, C_i\bar{v}_i(R - R_0)/QR_0(1 - R_0) \tag{A-7}$$

where i denotes the fraction number, $\bar{v}$ is the volume of the fraction, C is total concentration of isotopes, and Q is the total effective ion-exchange capacity of the isotopes treated. This equation was initially derived for the system where the separation column length is fixed and an isotope analysis was done on the effluent emerging from the column. On the basis of a different concept of isotopic migration in a homogeneous medium, Kakihana derived the same type of equation as Eq. (A-7) for the system where isotope distribution in the migration medium is known by direct sampling (*16*). In this case the amount of isotopes in the migration medium is used instead of the amount in the effluent, expressed by $C_i\bar{v}_i$ in Eq. (A-7).

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When the total concentration of isotopes is constant throughout the migration band and the sampling width is sufficiently narrow, that is, $C_i\bar{v}_i = C_0\Delta x$ and $Q = C_0L$, Eq. (A-7) is rearranged to

$$\varepsilon = \int_0^L (R - R_0)dx/LR_0(1 - R_0) \tag{A-8}$$

Combining Eqs. (A-6) and (A-8), we obtain

$$g = (e^{\varepsilon k R_0 L} - 1)/(1 - R_0)$$

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