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THEORY OF ISOTOPE SEPARATION BY DISPLACEMENT CHROMATOGRAPHY

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SUMMARY

Theoretical aspects of isotope separation are discussed for the steady-state and intermediate (non-steady-state) stages of the displacement chromatography of two isotopes. It is shown that the steady-state solution can be used even for the non-steady state to some extent. The theory could provide a basis for a feasibility study of an isotope separation process.

INTRODUCTION

Ion-exchange chromatography has been applied successfully to the separation of isotopes of various elements. In 1955, Spedding et al.[1] enriched ^{15}N to 74% from its original value of 0.365%. Based on a fundamental study by Kakihana et al.[2], Aida et al.[3] enriched ^{10}B from about 20% to over 98% using a weakly basic anion-exchange resin. Under the initial guidance of Kakihana, Seko et al.[4] at Asahi Chemical Industry are investigating a ^{235}U enrichment process using the redox reaction between U^{IV} and U^{VI} with the aim of achieving the commercial production of fuel-grade uranium. Other elements whose isotope separation by ion-exchange chromatography has been studied include lithium[5], carbon[6], magnesium[7], sulphur[8], calcium[9] and rubidium[10].

In parallel with experimental investigations, theoretical studies on the ion-exchange chromatographic separation of isotopes have been developed. Theoretical interest in this field is roughly divided into two aspects: equilibrium isotope effects or isotope distributions between the external solution phase and the resin phase, and isotope accumulation processes, *i.e.*, how isotopes are separated or how isotope separations proceed during chromatographic operations.

Theoretical consideration of equilibrium isotope effects concerns the determination of the isotopic reduced partition function ratios (RPFRs) of the species involved in the separation reactions and the consideration of the isotope distribution between the two phases. The RPFR is an essential quantity in the field of isotope chemistry and was introduced by Bigeleisen and Meyer[11]. Experimentally obtained single-stage separation factors, *S*, can be related to the RPFRs of the species involved in separation processes by the isotope two-phase distribution theory developed by Kakihana and Aida[12].

For the description of isotope accumulation processes, several investigators have proposed different theories. Glueckauf[13] tried to describe the isotopic behaviour in a chromatographic separation column based on the concept of "theoretical plates". Shimokawa[14], Jacques[15] and Fujine[16] independently applied Cohen's cascade theory[17] to column chromatographic separations of isotopes. Fujii *et al.*[18] gave an approximate equation that expresses isotopic behaviour in the non-steady state.

This paper concerns the second category of theoretical interest, *i.e.*, isotope accumulation in a separation column during chromatographic operation. We limit our discussion to the displacement chromatography of two isotopes. Despite the current availability of high-speed computers for the simulation of separation processes, analytical treatments are still very important and instrumental in avoiding the "black box", *i.e.*, computerized solutions of the mathematical models for chromatography expressed in the forms of partial differential equations. They could also provide a direct link between physical quantities of the isotopes such as diffusion coefficients and operational modes and the isotope separation performance of isotope separation equipment.

· About 12 years ago, we derived a fundamental equation for chromatography[19] and, by solving it under appropriate boundary conditions, obtained expressions for isotopic behaviour in chromatographic columns. Unfortunately, however, they can be applied only to the early stage of chromatography[20,21]. In this paper, starting with the fundamental equation[19], we first derive a material balance with a moving axis and obtain the steady-state solution and then discuss isotopic behaviour at the intermediate stage of displacement chromatography.

The fundamental equation for chromatography, which describes the behaviour of a species i in a column, is expressed as[19]

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x}\left(D_i \cdot \frac{\partial c_i}{\partial x}\right) - \frac{\partial}{\partial x}(v_i c_i) \tag{1}$$

where c_i is the concentration of the species i at position x fixed to the column and time t, D_i the chromatographic diffusion coefficient of the species i, an index representing all mass-transfer effects caused by concentration gradients in and between the solution and the resin phases along the x axis[22], and v_i the velocity of the species i due to external forces.

FUNDAMENTAL EQUATION FOR TWO-ISOTOPE SYSTEMS WITH CONSTANT TOTAL CONCENTRATION EXPRESSED ON A MOVING AXIS

We consider displacement chromatography of an element whose isotopes A and B are to be separated. In band operation, a band of the isotopes is preceded and followed by other bands (or zones) that do not contain the isotopes concerned. Sharp and stable boundaries (so-called self-sharpening boundaries) are formed at both ends of the band at the very beginning of the operation. During the operation, the band width is kept constant and the concentration of the element (the total concentration of the isotopes A and B) is also constant throughout the band. As the band is being developed at a constant velocity, isotopic fractionation takes place in the band owing mostly to a small difference in mobility and partly to a difference in diffusivity between

the two isotopes. In breakthrough and reverse breakthrough operations, the situation is similar to that of band operation except that the self-sharpening boundary is formed at one end of the chromatographic zone of the element and an infinitely large reservoir is attached at the other end of the zone.

Bearing the general picture of displacement chromatography above in mind, we consider idealized displacement chromatography, in which the boundary is extremely sharp and thus its width is assumed to be zero. The condition of displacement chromatography of two isotopes is expressed as

$$c_A + c_B = c \ (= \text{constant}) \tag{2}$$

or, in terms of the isotopic molar fractions of A and B, R_A and R_B, as

$$R_A + R_B = 1 \tag{2'}$$

Without losing generality, we also assume that A moves faster than B ($v_A > v_B$), that is, A will be enriched in front part of the band.

For the purpose of this work, it is convenient to express a fundamental equation using an axis that is moving with the band instead of using the x axis. We introduce a new coordinate z that is moving towards the positive x-direction at a velocity v at which the band moves:

$$z = x - vt \tag{3}$$

v can be related to v_i and D_i ($i = $ A, B) by the equation

$$(c_A + c_B)v = v_A c_A + v_B c_B - \left(D_A \cdot \frac{\partial c_A}{\partial z} + D_B \cdot \frac{\partial c_B}{\partial z} \right) \tag{4}$$

This equation means that the sum of the fluxes of A and B (right-hand side) is equal to the flux as a whole. With the help of eqns. 2, 2', 3 and 4, eqn. 1 can be rearranged into

$$\frac{\partial R_A}{\partial t} = \frac{\partial}{\partial z}\left(D_{AB} \cdot \frac{\partial R_A}{\partial z} \right) - \frac{\partial}{\partial z}(\Delta v R_A R_B) \tag{5}$$

where D_{AB}, which can be termed the "effective" diffusion coefficient, is given by

$$D_{AB} = D_A R_B + D_B R_A \tag{6}$$

and

$$\Delta v = v_A - v_B \tag{7}$$

Eqn. 5 is a fundamental equation for two-isotope displacement chromatography expressed by using the moving axis z instead of x. Eqn. 6 represents the fact that diffusion in a binary system with a constant total concentration has a more significant contribution from diffusion of the minor component than from that of the manjor component.

STEADY-STATE BEHAVIOUR OF ISOTOPES

Under the steady-state condition that

$$\partial R_A / \partial t = 0 \tag{8}$$

and the boundary conditions that

$$R_A = R_A^0 \text{ and } R_B = R_B^0 \text{ at } z = z_0 \tag{9}$$

where R_A^0 and R_B^0 are the original values of R_A and R_B, respectively, and z_0 is a point in the band at which $R_A = R_A^0$ and $R_B = R_B^0$, and

$$\partial R_A / \partial z = 0 \text{ at } R_A = 1 \tag{10}$$

eqn. 5 can be solved to give

$$\ln[(R_A/R_A^0)^{D_A}/(R_B/R_B^0)^{D_B}] = \Delta v(z - z_0) \tag{11}$$

in which D_A, D_B and Δv are assumed to be constant.
By introducing a new parameter defined by

$$\Delta D = D_A - D_B \tag{12}$$

eqn. 11 is rearranged into

$$\ln[(R_A/R_A^0)/(R_B/R_B^0)] + \frac{\Delta D}{D_A}[\ln(R_B/R_B^0)] = \frac{\Delta v}{D_A}(z - z_0) \tag{13}$$

Eqns. 11 and 13 are the steady-state solution of the fundamental equation. In eqn. 13, the magnitude of $\ln[(R_A/R_A^0)/(R_B/R_B^0)]$ is always larger than that of $\ln(R_B/R_B^0)$, as $R_A > R_A^0$ and $R_B < R_B^0$ for $z > z_0$ and $R_A < R_A^0$ and $R_B > R_B^0$ for $z < z_0$, and obviously $|\Delta D/D_A| \ll 1$. Hence the second term of the left-hand side of eqn. 13 is always less important than the first term. When the second term is negligibly small, eqns. 11 and 13 are simplified to

$$R_A/R_B = (R_A^0/R_B^0)\exp[k^*(z - z_0)] \tag{14}$$

where

$$k^* = \Delta v/D_A \tag{15}$$

Eqn. 14 shows that $\ln(R_A/R_B)$ is a linear function of z. The sharpness of the slope of the isotope accumulation curve is determined by k^*, which is termed the slope coefficient at the steady state. Several workers have derived expressions for the steady-state isotope distribution in displacement chromatography similar to eqn. 14, which in our theoretical treatment is derived as an approximation of eqn. 11.

To visualize eqns. 11 and 13, in Fig. 1 $\ln(R_A/R_B)$ is plotted against $z - z_0$ according to eqn. 13 (cases with $v_B > v_A$ are also included). Parameter values are not designed to represent any specific separation systems. $\Delta D/D_A = -0.2$ and 0.2 may be too large for isotopes of an element and are chosen only to show the effect of ΔD on the accumulation curve clearly. The curves at $\Delta D/D_A = 0.0$ correspond to those expressed by eqn. 14. As shown in Fig. 1, eqn. 14 is an excellent approximation of eqns. 11 and 13 in most practical cases of isotope separation, although this is not necessarily so with separations of elements or chemical species. If we can carry out a very precise experiment on chromatographic isotope separation, we may be able to estimate the value of ΔD by a best-curve fitting of the obtained results to eqn. 13.

Mathematically, the steady state is reached asymptotically as time proceeds. In band operation, we may assume that the steady state has been reached after a certain length of chromatographic development. Various factors affect the time spent to reach the steady state. For given parameter values in eqn. 11, for instance, it will be longer for a longer band width than for a shorter band width. Once the steady state has been attained, eqn. 11 holds throughout the band and the point $z = z_0$ exists somewhere within the band; this point can be determined from a material balance. The maximum degree of enrichment is obtained at one end of the band and the maximum degree of depletion at the other end, and further enrichment or depletion is never realized. In breakthrough or reverse breakthrough operation, the steady state is never attained, because there are always influxes of isotopes A and B into the separation column.

NON-STEADY STATE (INTERMEDIATE STAGE) OF DISPLACEMENT CHROMATOGRAPHY

In principle, the isotopic behaviour in a column at the intermediate, non-steady-state stage of displacement chromatography can be expressed by the time-dependent
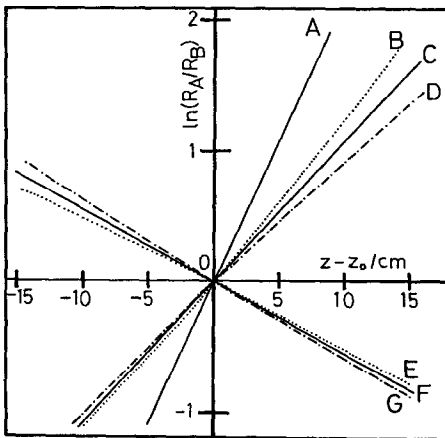

Fig. 1. Plots of $\ln(R_A/R_B)$ against $z - z_0$ for $R_A^0 = R_B^0 = 0.5$. The parameter values for each curve are as follows (Δv is in units of cm/s and D_A is in units of cm^2/s): (A) $\Delta v = 2.50 \cdot 10^{-6}$, $D_A = 0.5 \cdot 10^{-5}$, $\Delta D/D_A = 0.0$; (B) $\Delta v = 2.50 \cdot 10^{-6}$, $D_A = 1.0 \cdot 10^{-5}$, $\Delta D/D_A = 0.2$; (C) $\Delta v = 2.50 \cdot 10^{-6}$, $D_A = 1.0 \cdot 10^{-5}$, $\Delta D/D_A = 0.0$; (D) $\Delta v = 2.50 \cdot 10^{-6}$, $D_A = 1.0 \cdot 10^{-5}$, $\Delta D/D_A = -0.2$; (E) $\Delta v = -1.25 \cdot 10^{-6}$, $D_A = 1.0 \cdot 10^{-5}$, $\Delta D/D_A = -0.2$; (F) $\Delta v = -1.25 \cdot 10^{-6}$, $D_A = 1.0 \cdot 10^{-5}$, $\Delta D/D_A = 0.0$; (G) $\Delta v = -1.25 \cdot 10^{-6}$, $D_A = 1.0 \cdot 10^{-5}$, $\Delta D/D_A = 0.2$.

solution of eqn. 5. Unfortunately, it is extremely difficult to solve it analytically except for some very simple cases.

Glueckauf[13] proposed empirical equations describing the non-steady-state behaviour of isotopes. Fujii et al.[18] derived an expression describing the isotopic behaviour at the non-steady state under the assumption of a momentary steady state. Majumdar's theory of isotope separation by thermal diffusion[23] may be applied to displacement chromatography. Klemm[24] applied and extended Majumdar's treatment in an isotope accumulation theory for electromigration in molten salts. The most popular method for treating the intermediate stage is the numerical analysis as exemplified by that of Fujine[16]. Numerical solutions of eqn. 1 for multi-component systems under displacement operation were given by Oi et al.[25].

Although the analytical solution that can be applied to the whole range of the adsorption band of the isotopes to be separated at any given time is very difficult (or seems impossible) to obtain, an approximate expression is possible for a limited range of the band. At the boundary (the front end of the band in the case of breakthrough operation, the rear end in the case of reverse breakthrough operation and both the front and rear ends in band operation), the fluxes of isotopes A and B are each zero on the moving axis z at any stage of displacement chromatography. Mathematically, this is expressed as

$$D_{AB}\partial R_A/\partial z - \Delta v R_A R_B = 0 \tag{16}$$

Eqn. 16 is nothing but what is obtained under the steady-state condition in eqn. 8 and the boundary condition in eqn. 10. This means that at the boundaries, the steady-state solution in eqn. 11 (and in eqn. 13) or its approximate form (eqn. 14) holds at any stage.

In breakthrough operation, the isotopic fluxes will be nearly zero in the region that just follows the boundary. In practice, we may regard this region as being at the steady state. As the separation proceeds, the range of this region will increase. In reverse breakthrough operation, an analogous consideration can be applied to the region that just proceeds the boundary. In band operation, considerations on breakthrough and reverse breakthrough operations can be applied to the front and rear regions of the band, respectively.

A study on boron isotope separation by Sakuma et al.[26] provides an experimental example of this aspect. They separated boron isotopes by ion-exchange chromatography using the reverse breakthrough technique with a weakly basic anion-exchange resin as ion exchanger and distilled water as the eluent (in this instance, A = ^{11}B and B = ^{10}B). In Fig. 2, their data are plotted in the form of R_{B-10}/R_{B-11} vs. the distance from the rear end of the boron adsorption band. It can be clearly seen that $\ln(R_{B-10}/R_{B-11})$ is, to a good approximation, a linear function of distance in the region where its value is larger than about 0.9 (R_{B-10} = 0.45). The width of the range where linearity holds is about 20 cm for the 64-m migration experiment and about 50 cm for the 256-m migration experiment. We can say that in this specific system of boron isotope separation, eqn. 14 is applicable, at least in practice, to the region where $R_{B-10}/R_{B-11} \geqslant 0.9$.
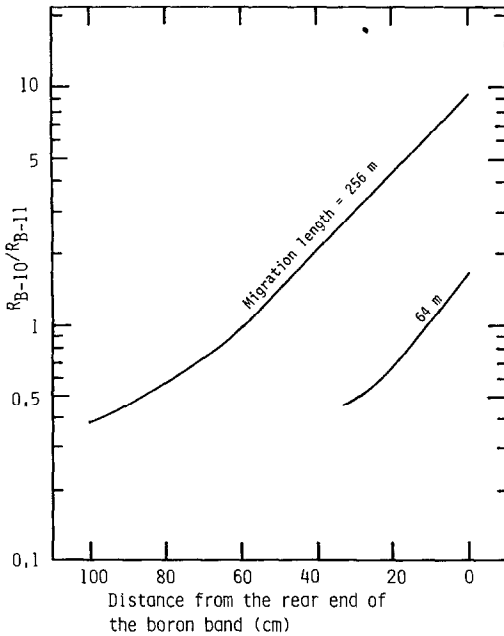
Fig. 2. Experimentally obtained accumulation curves of boron isotopes. Data from ref. 26.

POSSIBLE EXTENSION OF THE STEADY-STATE SOLUTION TO THE DESCRIPTION OF THE NON-STEADY STATE

The above example of boron isotope separation suggests that the steady-state solution can generally be used, to a good approximation, in the region where isotope enrichment proceeds over a certain level. The region where eqn. 11 or 14 can be applied would increase relative to the region where the non-steady-state solution, which is still unknown, should be applied, as the separation proceeds. After a sufficiently long time has elapsed since the beginning of an operation, the assumption that eqn. 11 or 14 holds for the whole region of the band in which an isotope, say A, is enriched would become a good one. We term the region where $R_A > R_A^0$ the enriched part. For such cases, we can derive expressions for a few important parameters when estimating the isotope separation performance of isotope separation equipment.

As was stated above, eqn. 14 is a good approximation of eqn. 11 in most practical cases of isotope separation. In the following, we use the approximate form of the steady-state solution (eqn. 14) in place of eqn. 11. First, we define several new parameters:

$$y = z - z_0 \tag{17}$$

$$r^0 = R_A^0 / R_B^0 \tag{18}$$

$$r_p = R_A^{product} / R_B^{product} \tag{19}$$

and

$$\Delta R_A = R_A^{\text{product}} - R_A^0 \tag{20}$$

where R_A^{product} is the molar fraction of R_A required for the product ($R_B^{\text{product}} = 1 - R_A^{\text{product}}$). With these parameters, eqn. 14 is rearranged into

$$R_A = [r^0 \exp(k^*y)]/[1 + r^0 \exp(k^*y)] \tag{21}$$

Width of the enriched part (y_p) required to obtain the product with r_p

This parameter is important in determining the width of the band required to obtain the product with the required enrichment and, consequently, in determining the scale of the separation equipment. y_p can be obtained from eqns. 19 and 21 as

$$y_p = (1/k^*) \ln(r_p/r^0) \tag{22}$$

As is seen in eqn. 22, a larger y_p value is needed for the higher degree of enrichment required for the product and a larger k^* value is preferable.

Start-up time (t_s)

The start-up time is the time elapsed between initiation of the chromatographic operation and the beginning of the production stage at which a product with the desired degree of enrichment can be withdrawn continuously or semi-continuously from one end of the band (the front end in this instance). Once production has commenced, t_s has no significant meaning. In practice, it should of course be minimized.

An expression of t_s can be derived from a consideration on the single-stage separation factor (S), one of the most fundamental quantities in the chromatographic separation of isotopes, which is defined as

$$S = ([\bar{B}]/[\bar{A}])/([B]/[A]) \tag{23}$$

where $[i]$ and $[\bar{i}]$ ($i = A, B$) are the amounts (moles) of i in the solution phase and in the resin phase, respectively. S can be expressed in terms of experimentally measurable quantities as[27]

$$S = 1 + [\int f(R_A - R_A^0)dy]/[R_A^0(1 - R_A^0)Q] \tag{24}$$

where f is the sum of the amounts of isotopes A and B per unit column length, Q is the total capacity of the column with respect to A and B from the start of the operation until time t and is related to f by

$$Q = fvt \tag{25}$$

and the integration is carried out over the whole of the enriched part. Using eqns. 21, 24 and 25, we can obtain the expression for t_s as

$$t_s = \int_0^{y_p} (R_A - R_A^0) dy / [R_A^0 (1 - R_A^0) \varepsilon v]$$

$$= [R_B^0 \ln(R_B^0 / R_B^{product}) - R_A^0 \ln(R_A^{product} / R_A^0)] / [R_A^0 (1 - R_A^0) \varepsilon k^* v] \qquad (26)$$

where $\varepsilon = S - 1$. As is seen, t_s is inversely proportional to ε, k^* and v.

Rate of growth of the enriched part (dy_e/dt)

The rate of growth of the enriched part at the production stage directly affects the amount of product withdrawn, since dy_e/dt miultiplied by c and the cross-sectional area of the column is the amount of product obtained per unit time when the product is withdrawn from the band continuously. dy_e/dt can be obtained by differentiating eqn. 27 with respect to t,

$$\int_0^{y_p} \Delta R_A^{product} dy = R_A^0 (1 - R_A^0) v \varepsilon t \qquad (27)$$

as

$$dy_e/dt = R_A^0 (1 - R_A^0) \varepsilon v / \Delta R_A^{product} \qquad (28)$$

Thus, dy_e/dt is a linear function of ε and v and is independent of k^*. A comparison of eqn. 28 with the result in a previous paper[20] (in which dy_e/dt was written as dx_e^*/dt) reveals that dy_e/dt is independent of the mathematical form of the isotope accumulation curve, that is, once the production stage has commenced the production rate is independent of the shape of the accumulation curve.

As a numerical example of eqn. 26, if we choose $\varepsilon = 7 \cdot 10^{-4}$, $v = 2$ m/h, $k^* = 0.05$ cm^{-1}, $R_A^0 = 0.0072$ and $R_A^{product} = 0.95$, modelling 95% ^{235}U enrichment from the natural uranium by the $U^{IV}-U^{VI}$ redox process[4], t_s is about 7 years. This value and values estimated for 3% ^{235}U enrichment[21] indicate that the chemical $U^{IV}-U^{VI}$ redox process is suitable for low enrichment but not for high enrichment of ^{235}U. The result that t_s is fairly long for high enrichment, coupled with the criticality problem, an intrinsic property of chemical chromatographic processes for ^{235}U enrichment[28], implies that a ^{235}U enrichment plant based on the $U^{IV}-U^{VI}$ redox process has a potentially high proliferation resistance.

Values of various parameters appearing in eqns. 22, 26 and 28 are predetermined or can be determined by small-scale chromatographic experiments. Therefore, given as explicit functions of these parameters, the equations are easy to use to evaluate the performance of isotope separation equipment with a minimum of experimental data. To the best of our knowledge, the theoretical treatment in this paper is the first to provide analytical results of a quantity such as dy_e/dt for the transient stage of displacement chromatography. It could be used as a basis for a feasibility study of an isotope separation process.

The validity of our treatment should, of course, be examined in comparison with experimental results. Unfortunately, however, no appropriate experimental data are available for this purpose at present, and the development of the necessary experimental work is desirable.

CONCLUSION

There is in practice a great demand for a means of analysing the results of experiments on displacement chromatographic separation of isotopes that have been done and of predicting results of experiments that are to be done. Although the present theory is still far from being established, it could provide such a means.

At the steady state, the ratio of the isotopic molar fraction of the two isotopes is, to a good approximation, an exponential function of the position. By curve fitting of the results of a very carefully performed experiment, the isotopic difference in diffusivity may be determined.

The analysis of the intermediate stage of displacement chromatography is important. Unfortunately, it is very difficult to obtain analytical solutions for this stage, which are strongly required even in approximate forms. It was shown that a solution similar to that of the steady state can be applied to a limited region of the isotope adsorption band and that the range of its applicability increases with increasing time.

This theory could be a basis for a feasibility study of an isotope separation process; with minimum fundamental data on the isotope enrichment performance of the process, important parameters such as y_p, t_s and dy_e/dt can be estimated.

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