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# Theoretical Study of Lithium Isotope Separation by Displacement Chromatography

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## Abstract

Lithium isotope separation by displacement chromatography is studied using fundamental principles; the equations are derived assuming theoretical stages in lithium adsorption bands. The concentration profiles in the band are calculated numerically under unsteady state.

## INTRODUCTION

Recently, the isotope separation technique by displacement chromatography has been advanced for uranium (*1*) and lithium (*2, 3*). Feasibility studies on the industrial production of isotopes are now being made. As to the fundamental characteristics of displacement chromatography, however, opinions among investigators differ (*4–8*). Even a small difference in theoretical considerations can seriously affect plant design.

Spedding analyzed experimental data of nitrogen isotope separation using Fenske's equation for the distillation theory. However, the details were not described (*4*).

Glueckauf assumed "chromatographic theoretical stages" in columns which have twice the height of the theoretical stage which would be obtained from the distillation-type model (*5*). He considered that the concentrations in the stages were uniform in their solid and liquid phases and were in equilibrium. He also assumed that the flow of liquid in columns was continuous; nevertheless, the solid phase was discontinuous. The solutions for isotope concentration profiles of the frontal processes were obtained under sharp boundary conditions. His assumption resulted in the introduction of an unreasonable "effective separation factor" into the equations. We consider Glueckauf's chromatographic model to be contradictory to the idea of the theoretical stage.

Kakihana assumed differential contact between the phases in the columns, and gave the fundamental equation represented by the terms of chromatographic movement and chromatographic diffusion peculiar to the species (*6*). If the term for chromatographic diffusion is omitted from the equation, it becomes the expression of the principle of elution chromatography; that is, the differences of the distribution coefficients cause the differences of the moving speed of the components in the columns, as described by DeVault (*9*). If the moving speed is constant and peculiar to the component, and also if the reflux operation at both ends of the band is not considered, the steady state never exists as in elution chromatography. He analyzed the separation characteristics of displacement chromatography for the case where the plateau of concentration remains at the center of the band, assuming the concentration profile to be of exponential form (*10*). However, the steady state exists for displacement chromatography and the concentration profile at the steady state is important for designing a plant for isotope separation.

Shimokawa applied Cohen's theory of two-phase separation by countercurrent with reflux operation to displacement chromatography. Solutions were obtained for frontal processes and band displacement for the case where the isotope concentration at the center of the band does not change during the displacement operation. He indicated that the reflux operation at the ends of the band had not been strictly treated by conventional theories (*7*). Jacques also gave solutions of the cascade theory for the frontal processes to evaluate HETP by analyzing experimental data (*8*). Their cascade theories are promising; however, the solutions are limited to special conditions.

Industrial lithium isotope separation should be carried out with equipment composed of several chromatographic columns in order to move an adsorption band continuously over a long distance. The isotope concentration profiles in the band are nearly at the steady state, and the plateau of concentration does not exist in the band at the optimum running conditions. Therefore, broader features of chromatography must be investigated than in past reports. For the purpose of evaluating the performance of lithium isotope separation, we will study the principles of displacement chromatography, derive equations assuming theoretical stages in lithium adsorption bands, and calculate the concentration profiles under unsteady state.

## COMPARISON BETWEEN DISPLACEMENT CHROMATOGRAPHY AND ELUTION CHROMATOGRAPHY

The principles of displacement chromatography and elution chromatography are the same in their utilization of the differences in distribution coefficients among solutes. However, the multiplication procedures of the differences are very different between these techniques.

In elution chromatography the differences in the moving speed of solutes, which are caused by the differences in distribution coefficients, are integrated in chromatographic columns. If two solutes have a large difference in distribution coefficients and are developed in a sufficiently long column, each peak of the solutes is separated completely and the interval between the two peaks becomes greater as elution proceeds. Therefore, steady state does not exist in this case. In order to realize elution chromatography, the following conditions are required. An eluent in the mobile phase must not have any interaction with the stationary phase; it only carries the solutes through the chromatographic column. In addition, the stationary phase must not be saturated by the solutes.

On the other hand, displacement chromatography is achieved by use of the saturation characteristics of the stationary phase. The operation is shown in Fig. 1. First, species E of the smallest distribution coefficient is adsorbed in a column. An adsorption band is formed at the top of the column with the addition of a mixed sample of components A, B, and C. Then the band is moved by species D of the largest distribution coefficient, keeping a constant band length. Each component is arranged in order of the distribution coefficients in the band. In contrast with elution chromatography, the components are never separated from each other but move together in

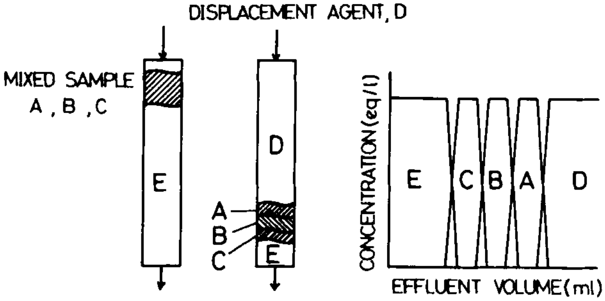

FIG. 1. Displacement chromatography.

contact with the adjoining components. When the arrangement is finished, steady state is attained and further displacement is not profitable. The concentration profiles at the steady state are determined by the relative distribution coefficients, the amounts of the components in the band, and the separation performance of the chromatographic columns.

## MOVING SPEED OF ADSORPTION BAND IN DISPLACEMENT CHROMATOGRAPHY

Consider the separation of lithium isotopes, $^6$Li and $^7$Li, by ion-exchange resins. As shown in Fig. 2, a strong-acid cation-exchange resin is conditioned into the H form and loaded with lithium, which is moved by Na ions. The order of selectivity coefficients ($K$) for the resin is $Na^+ > H^+ > Li^+$. When sodium acetate or hydroxide solution is used for the displacement agent, however, the following reaction occurs at the front boundary of the lithium band:

$$R{-}H^+ + Li^+ + CH_3COO^- \overset{K \gg 1}{\rightleftharpoons} R{-}Li^+ + CH_3COOH$$

or

$$R{-}H^+ + Li^+ + OH^- \overset{K \gg 1}{\rightleftharpoons} R{-}Li^+ + H_2O$$

where R is the ionic group in the resin. Therefore, the selectivity order changes to $Na^+ > Li^+ > H^+$. Thus the chromatographic operation is started at the same ion arrangement as for the steady state. The separation coefficients of Na—Li and Li—H at the boundaries of the lithium band are

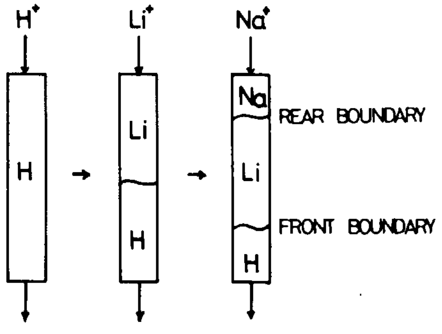

FIG. 2. Lithium isotope separation by displacement chromatography.

so large that the concentration profiles are rapidly settled to the steady state. On the other hand, since the separation coefficients of the lithium isotopes are very close to unity, the band needs to be moved over a long distance to attain steady state in the band.

In principle, a single component cannot exclusively occupy a part of the column. However, when the separation coefficient is large, the concentration change is restricted within a narrow limit of the column, and outside that limit the solution can be considered to be composed of a single component from a practical point of view. This part of the column, in which minor components can be neglected, is called an adsorption band. The quantity of ion in the band in a unit bed volume is equal to the ion-exchange capacity $q_0$ (eq/cm$^3$), and the quantity of the ion in a unit liquid volume is equal to the concentration of displacement agent $C_0$ (eq/cm$^3$). Therefore, the ratio between the quantities of both phases, namely, the distribution coefficient $D_v$, becomes

$$D_v = q_0/C_0 \tag{1}$$

This value does not depend on the species. It is clear that the moving speed of the band also does not depend on the species.

Lithium moves in the column, keeping a constant band length, and reflux occurs at the boundaries of the band. Lithium isotope concentration profiles begin to be formed in the vicinity of the boundaries by the reflux effect, similar to a distillation column. The profile extends to the center of the band and, at last, steady state is attained.

## ISOTOPE CONCENTRATION PROFILES IN ADSORPTION BANDS

### Interstage Flow Rate

Imagine a plate in a lithium band as shown in Fig. 3, The plate moves at the same speed $U_B$ (cm/s) as the band. If the cross-sectional area of the column is unity (cm$^2$), the lithium quantity $L'$ (mol/s) which passes through the imaginary plate in the resin phase per unit time is expressed as

$$L' = q_0 U_B \tag{2}$$

The lithium quantity $L''$ (mol/s) which passes through the plate in the liquid phase per unit time is calculated by

$$L'' = C_0 \overline{U} - \varepsilon C_0 U_B \tag{3}$$

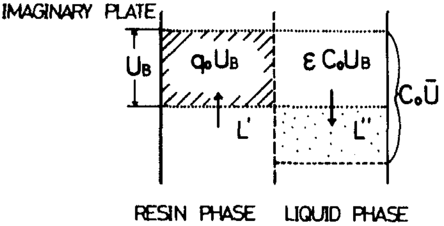

FIG. 3. Countercurrent in chromatographic column.

where $\overline{U}$ (cm/s) is the superficial velocity of the development agent and $\varepsilon$ is void fraction of the column. The latter term is added to correct for the movement of the plate. The following relation is derived from the material balance:

$$C_0\overline{U} = U_B(q_0 + \varepsilon C_0) \tag{4}$$

Equation (3) can be changed to

$$L'' = \frac{q_0 C_0}{q_0 + \varepsilon C_0}\overline{U} = q_0 U_B \tag{5}$$

Therefore, the following relation holds:

$$L' = L'' \tag{6}$$

This means that the lithium adsorption band can be regarded as a packed bed of the countercurrent type in total reflux operation.

In the packed bed of the ion-exchange resin there can be nonequilibrium between the resin and solution phases and nonuniform flow in the void of the bed. Therefore, a finite height $\Delta z$ (cm), in which the concentration is substantially uniform in each phase, can be considered with good reason. The height may be called a stage. If stages which move at the same speed $U_B$ as the band are assumed in the chromatographic column, the band can be considered to be a multistage distillation column with a countercurrent of upstream $L'$ and downstream $L''$.

## Holdup in Stages

Lithium holdup $H_0$ (mol) in a stage is expressed by

$$H_0 = (q_0 + \varepsilon C_0)\Delta z \tag{7}$$

When the concentration of lithium isotope $^6$Li is $q$ (mol/cm$^3$) in the resin phase and $C$ (mol/cm$^3$) in the liquid phase, $^6$Li holdup $H$ (mol) in a stage is expressed by

$$H = (q + \varepsilon C)\Delta z \tag{8}$$

If the stage is assumed as a "theoretical stage," the concentrations of both phases are in equilibrium. The isotope separation factor is defined as

$$\alpha = \frac{\bar{N}}{1 - \bar{N}} \bigg/ \frac{N}{1 - N} \tag{9}$$

where the isotope fractions $\bar{N}$ and $N$ are

$$\bar{N} = q/q_0, \qquad N = C/C_0 \tag{10}$$

and Eq. (9) is changed to

$$q = \frac{\alpha q_0 C}{C_0 + (\alpha - 1)C} \tag{11}$$

In the case of $\alpha \approx 1$, $C_0 \gg (\alpha - 1)C$ holds. Then

$$q \approx \frac{q_0}{C_0} C \tag{12}$$

Therefore, the holdup of the isotope in a theoretical stage is expressed by

$$\begin{aligned} H &= \left(\frac{q_0}{C_0} + \varepsilon\right) C\Delta z \\ &= H_0 N \end{aligned} \tag{13}$$

## Fundamental Equations

The material balance for a theoretical stage, shown at Fig. 4, is expressed by

$$H_0 \frac{dN_z}{dt} = L'(\bar{N}_{z-\Delta z} - \bar{N}_z) + L''(N_{z+\Delta z} - N_z) \tag{14}$$

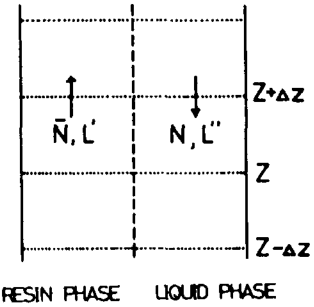

FIG. 4. Stage contact model in adsorption band.

When the dimensionless time $\tau$ is used,

$$\tau = \frac{L'}{H_0} t \tag{15}$$

Equation (14) can be written using the relation $L' = L''$ as follows:

$$\frac{dN_z}{d\tau} = (N'_{z-\Delta z} - N'_z) + (N_{z+\Delta z} - N_z) \tag{16}$$

Equation (9) for the definition of the isotope separation factor can be changed to

$$\bar{N} = \frac{\alpha N}{1 + (\alpha - 1)N} \tag{17}$$

or

$$\bar{N} = N + \frac{(\alpha - 1)N(1 - N)}{1 + (\alpha - 1)N} \tag{18}$$

Since we assume the same stage contact as for a multistage distillation column, $N_{z-\Delta z}$, $N_z$, and $N_{z+\Delta z}$ can be regarded as the mole fractions at the $(s-1)$th, $(s)$th and $(s+1)$th stages, respectively, and the suffix to $N$ is changed to $s$. Therefore, Eq. (16) is changed, using Eq. (18), as follows:

$$\frac{dN_s}{d\tau} = N_{s+1} - 2N_s + N_{s-1} - (\alpha - 1)\left\{\frac{N_s(1 - N_s)}{1 + (\alpha - 1)N_s} - \frac{N_{s-1}(1 - N_{s-1})}{1 + (\alpha - 1)N_{s-1}}\right\} \tag{19}$$

or, approximately,

$$\frac{\partial N}{\partial \tau} = \frac{\partial^2 N}{\partial s^2} - (\alpha - 1)\frac{\partial}{\partial s}\left\{\frac{N(1 - N)}{1 + (\alpha - 1)N}\right\} \tag{20}$$

When $1 \gg (\alpha - 1)N$ holds, then

$$\frac{\partial N}{\partial \tau} = \frac{\partial^2 N}{\partial s^2} - (\alpha - 1)\frac{\partial}{\partial s}\{N(1 - N)\} \tag{21}$$

This equation is the fundamental equation for displacement chromatography. The equation is rewritten using real time as follows:

$$H_0\frac{\partial N}{\partial t} = L'\frac{\partial^2 N}{\partial s^2} - (\alpha - 1)L'\frac{\partial}{\partial s}\{N(1 - N)\} \tag{22}$$

When the following replacements are made:

$$L = L' + L'' \tag{23}$$

$$2\varepsilon' = \alpha - 1 \tag{24}$$

Eq. (22) becomes

$$H_0\frac{\partial N}{\partial t} = \frac{L}{2}\,\frac{\partial^2 N}{\partial s^2} - \varepsilon' L\frac{\partial}{\partial s}\{N(1 - N)\} \tag{25}$$

Equation (25) is equal to the fundamental equation derived by Cohen for square cascades in a total reflux operation (*11*). $\varepsilon'$ is Cohen's enrichment factor (namely, the tail enrichment factor) and $2\varepsilon'$ is the total enrichment factor of a separation unit (namely, a stage). Therefore, by changing the physical meaning of the coefficients, the equations of Cohen's cascade theory are available for the calculation of the isotope concentration profiles in lithium adsorption bands, except for the short part at both ends of the band in which the lithium concentration changes.

The "effective separation factor" defined by Glueckauf does not appear in these equations. The finite differences of Eq. (16) can also be expressed by means of differentials, according to Taylor's theorem. The height of a theoretical stage $\Delta z$ is not infinitely small, and the concentration in the stage is assumed to be uniform in each phase. Therefore, the second differentials for both phases cannot be neglected. Thus the following equation is obtained:

$$\frac{1}{\Delta z}\frac{\partial N}{\partial \tau} = \frac{\Delta z}{2}\frac{\partial^2}{\partial z^2}(\bar{N} + N) - \frac{\partial}{\partial z}(\bar{N} - N) \tag{26}$$

In the case of $\alpha \approx 1$, Eq. (26) can be approximated as

$$\frac{1}{\Delta z}\frac{\partial N}{\partial \tau} = \Delta z\frac{\partial^2 N}{\partial z^2} - (\alpha - 1)\frac{\partial}{\partial z}\{N(1 - N)\} \tag{27}$$

This equation becomes equal to Eq. (21) using the relation $\partial z/\Delta z = \partial s$. On the other hand, neglecting the second differential for the liquid phase (which Glueckauf did neglect) leads Eq. (16) to a form which is different from the fundamental Eq. (21).

## Concentration Profiles at the Steady State

When the fundamental Eq. (21) is integrated at the steady state condition:

$$\partial N/\partial \tau = 0 \tag{28}$$

and at the boundary conditions:

$$\begin{aligned} N &= N_w, && \text{at } s = 0 \\ N &= N_p, && \text{at } s = S \\ \partial N/\partial s &= 0, && \text{at } N = 0 \text{ and } N = 1 \end{aligned}$$

then the following relation is obtained:

$$S = \frac{1}{\alpha - 1} \ln \frac{N_p(1 - N_w)}{N_w(1 - N_p)} \tag{29}$$

The approximation $\alpha - 1 \approx \ln \alpha$ holds for $\alpha \approx 1$. Therefore, Eq. (29) is equal to Fenske's equation:

$$S = \frac{\ln \dfrac{N_p(1 - N_w)}{N_w(1 - N_p)}}{\ln \alpha} \tag{30}$$

Fenske's equation also holds for a large separation factor if the separation factor is constant for each stage.

## Transient Behavior

The transient solutions of Eq. (25) have been given for special cases by Cohen (*11*). The more general transient profiles in lithium bands are calculated numerically as follows.

Figure 5 shows a lithium band as an imaginary distillation column or a

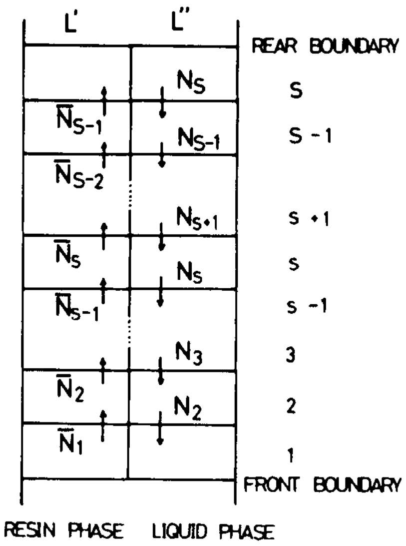

FIG. 5. The imaginary distillation column.

square cascade which is composed of many theoretical stages having identical separation coefficients. As the height equivalent to a theoretical stage $\Delta z$ is assumed to be uniform through the band, the total number of the theoretical stages $S$ can be related to the band length $l_B$ (cm) by

$$S = l_B/\Delta z \tag{31}$$

The bottom stage is adjacent to the front boundary and the top stage to the rear boundary. Both boundaries are assumed to be the plates vertical to the flow in the column.

The concentration changes are expressed using the dimensionless time $\tau$ for the top stage ($s = S$):

$$dN_s/d\tau = \bar{N}_{s-1} - N_s \tag{32}$$

for the arbitary stages ($s \neq 1, S$):

$$dN_s/d\tau = \bar{N}_{s-1} + N_{s+1} - \bar{N}_s - N_s \tag{33}$$

for the bottom stage ($s = 1$):

$$dN_1/d\tau = N_2 - \bar{N}_1 \tag{34}$$

And Eq. (17) is changed as follows:

$$\bar{N}(s) = A(s)N(s) \tag{35}$$

where

$$A(s) = \frac{\alpha}{1 + (\alpha - 1)N(s)} \tag{36}$$

Since the isotope concentration change per stage is very small, the functions of $N(s)$ and $A(s)$ can be approximated by the differentials of Taylor's expansion. The terms of the first and second differentials are used for $N(s)$ except for the ends ($s = 1, S$). Since the differential $\partial A(s)/\partial s$ is very small, the relation of $A(s) \approx A(s + 1)$ is assumed, and the following basic equations are obtained:

$$\frac{\partial N}{\partial \tau} = (1 - A)N - \frac{\partial N}{\partial s} \qquad (s = S) \tag{37}$$

$$\frac{\partial N}{\partial \tau} = \frac{1}{2}(A+1)\frac{\partial^2 N}{\partial s^2} + (A-1)\frac{\partial N}{\partial s} \qquad (s \neq 1, S) \qquad (38)$$

$$\frac{\partial N}{\partial \tau} = (A-1)N + A\,\frac{\partial N}{\partial s} \qquad (s = 1) \qquad (39)$$

Furthermore, the constancy of total holdup $H_T$ in the band gives the following condition:

$$dH_T/d\tau = 0 \qquad (40)$$

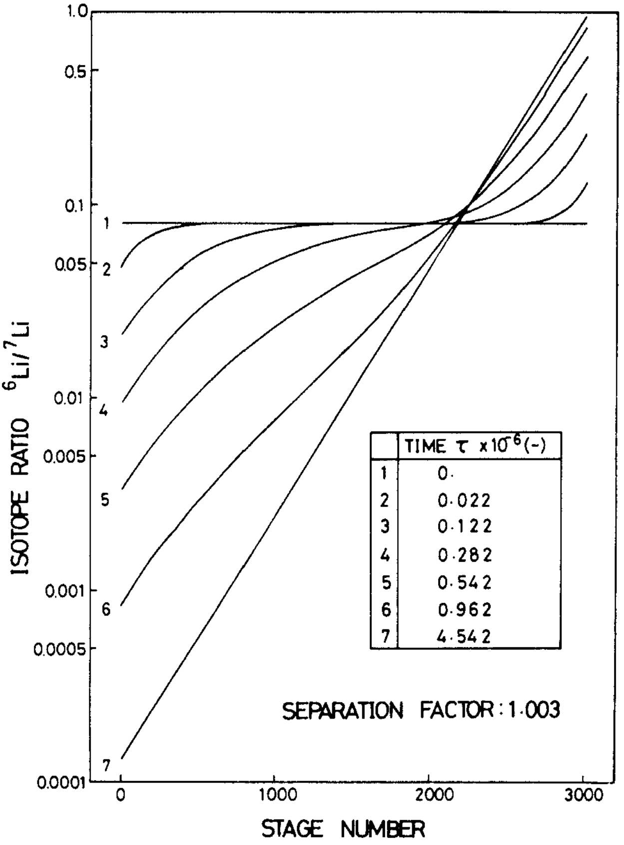

FIG. 6. Isotope concentration profiles in lithium adsorption band under unsteady state.

These equations are solved numerically in the same way described in a report about a gaseous diffusion plant (*12*): namely, the representative stages are chosen at regular intervals in the imaginary square cascade; the partial differentials of Eqs. (37), (38), and (39) are approximated by the finite differences using the concentration of the representative stages; and the linear differential equation system obtained is solved using the Runge-Kutta-Merson method.

Figure 6 shows the isotope concentration profiles calculated for the separation factor 1.003, the total theoretical stages 3000, and the natural lithium fed. The concentration profiles start to form at both boundaries and extend to the central part of the band, and, finally, the profile becomes linear on the semilogarithmic ordinate. The displacement moves the stage number of the initial isotope concentration from the center of the band to the 2170th stage at steady state. This phenomenon is caused by the limitation that the amounts of $^6$Li and $^7$Li are not equal. Figure 7 shows the transient concentration behavior of several stages for the same calculation conditions as for Fig. 6. The abscissa is the dimensionless time. The dimensionless time and stage number can be transformed into the real time and position in the lithium band using Eqs. (15) and (31), respectively.

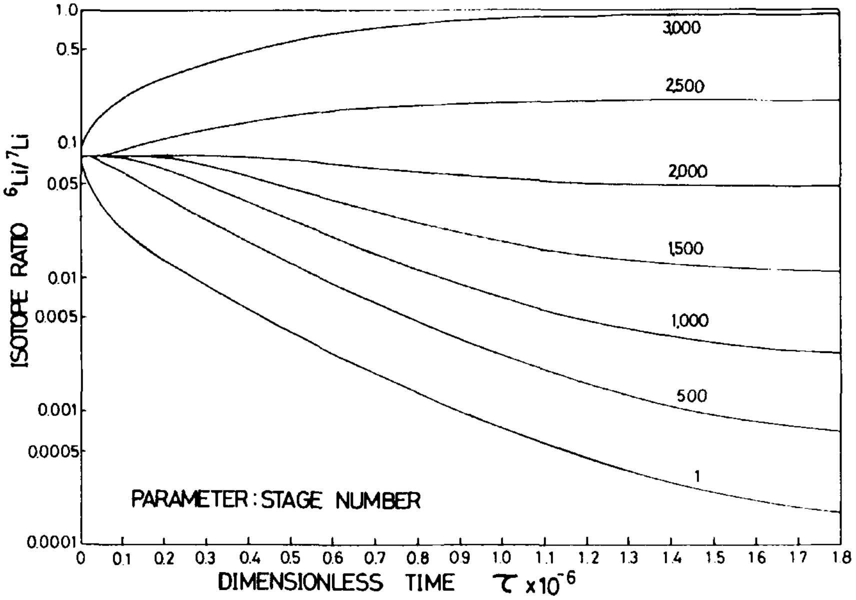

Fig. 7. Transient concentration behavior in the band.

## CONCLUSION

Lithium isotope separation by displacement chromatography was studied theoretically, and the following conclusions were obtained.

(1). The theories for distillation columns of the countercurrent contact type or square cascades in a total reflux operation are most reasonable for calculation of the concentration profiles in lithium adsorption bands.

(2). By assuming the theoretical stages in the bands, fundamental equations were derived which connect such important factors as the speed of the moving band, HETP, the interstage flow rates, the holdups in stages, the separation factors, the time, and the isotope concentrations of the stages. These equations also include those at the steady state, which have not been derived for displacement chromatography.

(3). The transient concentration profiles in the lithium band were calculated numerically without any limitation. The result showed that the stage of the initial isotope concentration moved from the center of the band to some other point during displacement.

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