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Journal of Chromatography A, 793 (1998) 223–230

JOURNAL OF
CHROMATOGRAPHY A

Flow-rate dependence of the height equivalent to a theoretical plate in nitrogen isotope separation by displacement chromatography

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Received 16 June 1997; received in revised form 8 September 1997; accepted 8 September 1997

Abstract

The effect of flow-rate in nitrogen isotope separation was studied for a wide range of fluid velocities using porous microreticular cation-exchange resin. The displacement chromatography was conducted from a band velocity of 6.3×10^{-3} to 12.5 cm/min (or Reynolds number of 15–30 000). A sharp adsorbed ammonium band was maintained even at a band velocity of 12.5 cm/min; on the other hand, tilted and/or channeled boundaries of the band are enlarged in the low-flow-rate region. The effect of fluid velocity on the height equivalent to a theoretical plate (HETP) of isotope separation was evaluated in terms of Reynolds number. In the present work, the HETP is proportional to the square-root of the band velocity in the turbulent flow regime and inversely proportional to the fluid velocity in the laminar flow regime due to the longitudinal mixing which is caused by tilting and/or channeling at the band boundary. © 1998 Elsevier Science B.V.

Keywords: Height equivalent to a theoretical plate; flow-rate; Displacement chromatography; Isotopes; Nitrogen

1. Introduction

Nitrogen isotope separation by ion-exchange chromatography has been studied since Spedding et al. [1] made experiments using a cation-exchange resin (Dowex 50-X12) in 1955. In recent years, ¹⁵N enrichment was investigated by Park and Michaels [2] and Kruglov et al. [3]. Park and Michaels intensively studied the effects of operating parameters on the height equivalent to a theoretical plate (HETP) using gel-type ion-exchange resin. The effects of resin size, temperature, eluent concentration, and superficial velocity were examined in their work. Kruglov et al. applied the SMB (simulated moving bed) process to the separation and

studied the influence of superficial velocity on HETP using macroreticular ion-exchange resin. In the work of Park and Michaels and Kruglov et al., linear relations between HETP and superficial velocity were confirmed.

The theoretical equations of HETP in the elution chromatography have been developed by Giddings [4], Huber and Hulsman [5], Kennedy and Knox [6], and Horváth and Lin [7], since Van Deemter et al. [8] first proposed the concept of rate theory for chromatography. The theoretical equations for isotope separation by displacement chromatography were derived by Glueckauf [9], Kakihana et al. [10], Shimokawa [11], and Fujine et al. [12]. In the equation of Fujine et al., the HETP of isotope separation is described as a sum of the terms of mass transfer in resin particles and liquid mixing, and proportional to the superficial

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velocity of displacement reagent and square of the resin particle diameter. This equation was found to agree well with their experimental data within their experimental conditions.

In this paper, the influence of flow-rate on the HETP is studied for a wide range of superficial fluid velocity using porous microreticular ion-exchange resin. Although previous studies [1–3] dealt with the effect of the flow-rate as one of the operating parameters, the fluid velocity of the experiments was restricted to the moderate flow-rate region in these works. In order to investigate the relation between fluid flow-rate and separation effect, a high-pressure-resistant glass column system is used in the present work.

2. Experimental (Table 1)

The sulfonated strong acid cation-exchange resin TITEC H-2 (porous microreticular type, particle size 77–177 μm , H^+ form) was packed uniformly in a pressurized glass column of 2 cm I.D. with a water jacket. The schematic of the separation column system used was described in a previous paper [13]. The ion-exchange resin in the column was preliminarily conditioned to the H^+ form with 2 *M* HCl solution. A solution of 1 *M* ammonia was fed to the column until an ammonium adsorption band was formed, and then the band was eluted by the displacing solution of 1 *M* NaOH in the reverse breakthrough manner. To feed HCl and NaOH solutions, titanium high-pressure pumps were used in this work. The superficial velocities (SVs) examined were 1.4×10^{-2} , 6.2×10^{-2} , 1.4×10^{-1} , 1.4, 14 and 27 cm/min and each of the migration distances was 86, 95, 95, 115, 115 and 115 cm, respectively. The column pressure observed was 10 kg/cm^2 (9.8×10^5

Pa) in the maximum flow-rate run (SV=27 cm/min). The effluent, which emerged from the column, was collected using a fraction collector. In order to prevent the NH_4OH samples from de-gassing, certain volumes of excess HCl solutions were added in the collection tubes prior to the samplings. The temperature of the column was kept constant at 298 K throughout the experiments by passing the thermostated water through the water jacket.

The concentrations of NH_4^+ in the fractions were determined by an Yokogawa-Hokushin IC-100 ion chromatography analyzer. The collected samples in the form of NH_4Cl were converted to N_2 gas for isotopic analysis by KBrO solution. The mass peaks of $^{14}\text{N}^{15}\text{N}$ and $^{14}\text{N}^{14}\text{N}$ of the samples were measured with an ESCO EMD-05S double focusing mass spectrometer and the isotopic abundance of ^{15}N was calculated from the ratio of the peak height.

3. Results and discussion

3.1. Separation coefficient

The elution curves and isotope distribution curves of four runs are shown in Fig. 1a–d as examples. It is seen that the ideal displacement chromatograms are obtained at high flow-rates; i.e. the sharp boundary between the ammonium band and the sodium band is maintained during the migration. On the contrary, tilted and/or channeled boundaries of the bands are enlarged at low flow-rates and found to increase with decrease in the fluid velocity. Since it is necessary to maintain the sharp ammonium band for long-distance migration in order to obtain highly enriched ^{15}N , the results clearly indicate that the chromatographic operation should be conducted at sufficiently high flow-rates.

The separation of nitrogen isotopes by means of

Table 1
Conditions

Ion-exchange resin: TITEC–H2 (sulfonated strong acid, porous microreticular type, crosslinking 20%, particle size 77–177 μm)
Temperature: 298 K
Eluent concentration: 1 <i>M</i>
Column diameter: 2 cm
Superficial velocity: 1.4×10^{-2} , 6.2×10^{-2} , 1.4×10^{-1} , 1.4, 14, and 27 cm/min
Migration distance: 86–115 cm

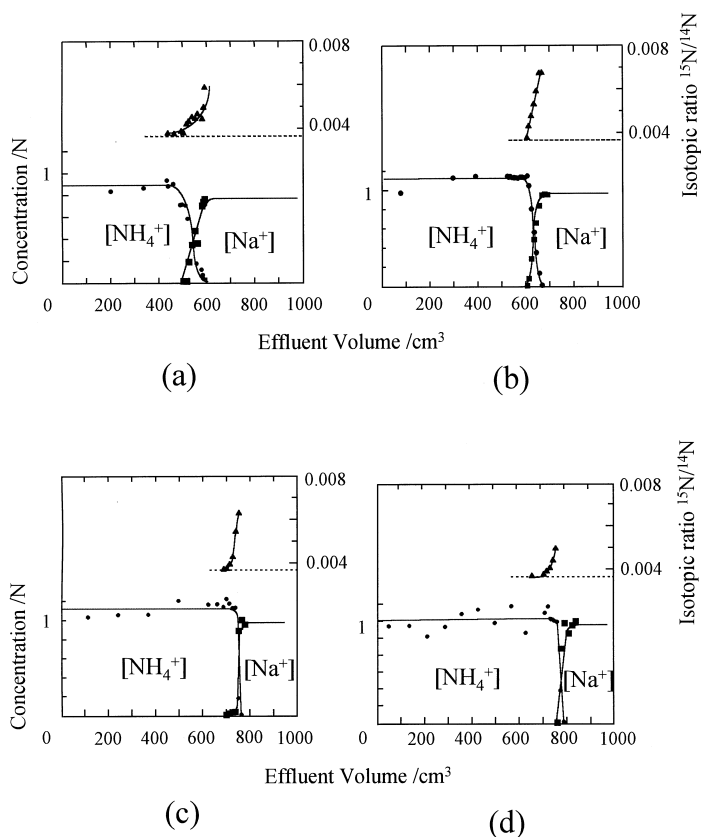


Fig. 1. Eluted ammonium band profiles and measured ^{15}N isotope concentration in the rear boundary regions at superficial velocities of 1.4×10^{-2} (a), 6.2×10^{-2} (b), 14 (c), and 27 cm/min (d).

cation-exchange resin is based on the isotopic fractionation between ammonia in aqueous solution and ammonium ion in the ion-exchange resin as shown below:



where R represents the fixed anion in the resin. The single-stage separation factor S or the separation coefficient ϵ is defined by

$$S = 1 + \epsilon = \frac{[\overline{{}^{15}\text{N}}][{}^{14}\text{N}]}{[{}^{15}\text{N}][\overline{{}^{14}\text{N}}]} \quad (2)$$

where $[\]$ denotes the concentration of isotopes in the aqueous phase and $[\overline{\ \ }]$ the concentration of the isotopes in the resin phase. The separation coefficients ϵ are determined by applying the experimental

data to the equation derived by Spedding et al. [1]. The calculated values are plotted in Fig. 2 as a function of the band velocity. It is confirmed in the figure that the separation coefficients are constant within experimental error in the range of band velocity from 6.3×10^{-3} to 12.5 cm/min. The average value of ϵ observed is 0.0201 ± 0.0010 . The result is reasonable since the chemical condition is unchanged in the experimental runs and a re-mixing of the enriched part and depleted part does not occur in this system. In the present work, the isotope accumulation in the rear boundary region was detected even on a migration velocity of 12.5 cm/min at 1 m migration. The result indicates that the isotopic exchange rate is significantly fast in this chemical system by using porous microreticular ion-exchange resin.

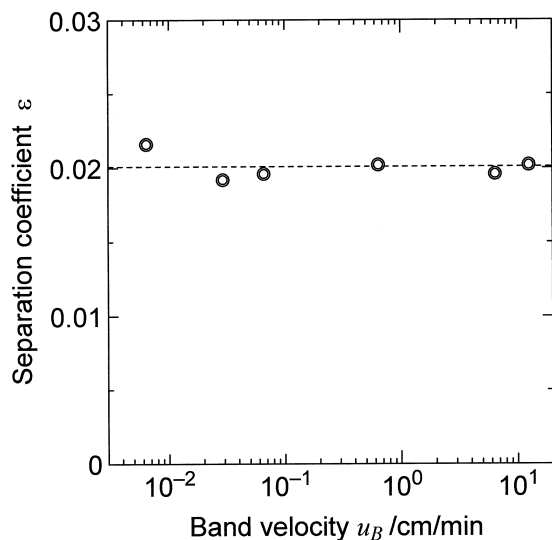


Fig. 2. Observed separation coefficients vs. band velocity.

3.2. HETP

In order to evaluate the performance of the ^{15}N enrichment in displacement chromatography, HETP is introduced. In a transient state, as in the case of the present work, HETP is usually obtained by a computer calculation fitting based on a cascade theory. However, in a previous paper, Fujii et al. [14] proposed more convenient equations to analyze chromatographic data on isotope separation. These equations are used in the present work. Thus, HETP is determined by the following equation for the transient state isotope separation.

$$H = \frac{\epsilon}{k} \left\{ 1 + \frac{R_0}{\exp(\epsilon k R_0 L) - 1} \right\} \quad (3)$$

When the enrichment extent is not so large, i.e. $\epsilon k R_0 L \ll 1$,

$$H = \frac{\epsilon}{k} + \frac{1}{k^2 L} \quad (4)$$

where H is the HETP, ϵ the separation coefficient, k the slope coefficient, R_0 the original isotope atomic fraction, L the migration length.

The observed HETP of each migration velocity is plotted in Fig. 3. It is seen in the figure that there is a linear relation between $\ln H$ and $\ln u_B$ with a slope of

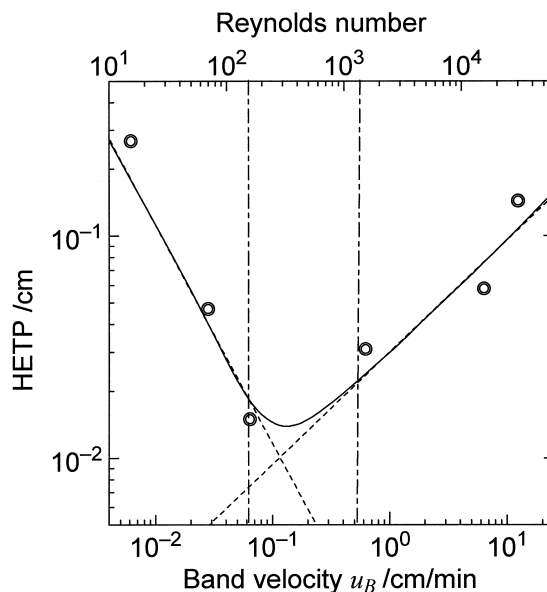


Fig. 3. Plots of HETP against band velocity and Reynolds number.

0.5 in the high flow-rate region; on the other hand, HETP reduces with increase in the fluid velocity with a slope of -1 at very low flow-rates in the present experiments. The result suggests that HETP is proportional to the square root of the band velocity in the range above ca. 0.5 cm/min (or superficial velocity greater than ca. 1.1 cm/min) and inversely proportional to the band velocity below the rate of ca. 6×10^{-2} cm/min (or superficial velocity less than ca. 0.1 cm/min). Thus, the following empirical relation is obtained.

$$H = \frac{a}{u_B} + b\sqrt{u_B} + c \quad (5)$$

where u_B is the band velocity and a , b , c the constant.

The HETP of the isotope separation is also evaluated using the Reynolds number. The Reynolds number is defined as,

$$\text{Re} = \frac{d u \rho}{\mu} \quad (6)$$

where d is the diameter of the flow path, u the average velocity of the fluid, ρ the fluid density, and μ the fluid viscosity. In the case of fluid flow in the cylindrical tube, these parameters are easily deter-

mined, however, a generalized formula is not established for the fluid flow through the packed column since the diameter of the flow path and the velocity of the fluid are not simply given. In the present work, the capillary model is adopted for the evaluation of the diameter of flow path in the experiment. In this model, the diameter of the flow path is given in terms of hydraulic radius. The diameter of flow path D_e and hydraulic radius R_h are defined as,

$$D_e = 4R_h, \quad (7)$$

$$R_h = \frac{\text{total void volume}}{\text{total surface area}} = \frac{\delta}{S_p(1-\delta)} = \frac{d_p \delta}{6(1-\delta)}$$

where δ is the void fraction and S_p the specific surface area; $S_p = 6/d_p$ for a sphere. The following parameters are used for the calculation: void fraction of resin bed, $\delta = 0.5$; diameter of the particles, $d_p = 0.01$ (cm); fluid density, $\rho = 0.99$ (g/cm³); fluid viscosity, $\mu = 8.9 \times 10^{-3}$ (g/cm s). Then the diameter of the flow path D_e is calculated as,

$$D_e = 6.68 \times 10^{-3} \text{ (cm)} \quad (8)$$

As the volumetric flow-rate Q (cm³/s) is given, the velocity of fluid in the flow path u_e is also determined.

$$u_e = \frac{4Q}{\pi D_e^2} \quad (9)$$

Using Eqs. (6)–(9), the Reynolds number is determined.

$$\text{Re} = \frac{D_e u_e \rho}{\mu} = 21445Q \quad (10)$$

The relation between Reynolds number, band velocity and HETP is shown in Fig. 3. In the figure, HETP is proportional to the square-root of the Reynolds number (or fluid velocity) in the turbulent flow regime ($\text{Re} > 2300$), on the other hand, it increases with the decrease in the Reynolds number when Re is below 150 in the laminar flow regime. Fig. 3 also shows that the critical Reynolds number of the system shifts slightly to the laminar flow region. The critical Reynolds number of 1300 is observed between the turbulent and transient flow regime in the figure.

As previously mentioned, tilted and/or channeled boundaries of the bands become large at low flow-rates. In this paper, HTU (height of a transfer unit) is considered in order to evaluate the longitudinal diffusion (or spreading of the band boundary) originating from the tilting and/or channeling in the reverse breakthrough chromatography. HTU is determined by the following equation using an ammonium concentration profile at the rear end of the band.

$$\text{HTU} = \frac{z}{\text{NTU}} = \frac{z}{\int_{y_1}^{y_2} \frac{dy}{y' - y}} \quad (11)$$

where y denotes the mole fraction of ammonium ion in the resin phase, y' the mole fraction at equilibrium with the mole fraction x in the liquid phase, z the distance between y_1 and y_2 , and NTU is the number of transfer units. The equilibrium constant is determined as follows using dissociation constant of ammonia ($\text{p}K_b = 4.76$).

$$K_{\text{NH}_4}^{\text{Na}} = \left(\frac{y}{1-y} \right) / \left(\frac{x}{1-x} \right) = 5.8 \times 10^4 \quad (12)$$

The operating line agrees with the diagonal $y-x$ graph. The graphic integration of the ammonium mole fraction from 0.05 to 0.95 gives the number of transfer units.

$$\text{NTU} = \int_{0.05}^{0.95} \frac{dy}{y' - y} = 2.94 \quad (13)$$

The observed HTUs are standardized to the values of 1 m migration since migration distances are different in each run. The relation between Reynolds number, band velocity and standardized HTU is shown in Fig. 4. In the figure, the HTU of the system is analogous to the HETP of the nitrogen isotope separation in Fig. 3 below a band velocity range of ca. 0.4 cm/min. On the other hand, HTUs are constant at 0.11 cm in the band velocity range above ca. 0.4 cm/min. Fig. 3 also shows that the longitudinal diffusion caused by tilting and/or channeling is negligible, and that the band boundary is sharp in the turbulent flow whereas tilted and/or channeled boundaries enlarge in the laminar flow regime. The results of Figs. 3 and 4 indicate that HTU (i.e. the longitudinal diffusion) decisively influences HETP and that the chromatographic operation should be conducted at the flow-

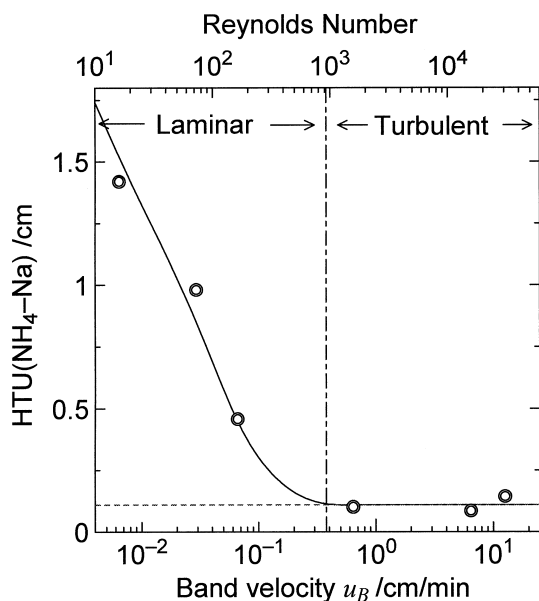


Fig. 4. Plots of standardized HTU against band velocity and Reynolds number.

rate in the turbulent flow regime in order to maintain a sharp boundary. The critical Reynolds number observed in Fig. 4 appears to be ca. 1000, and is identical to the value obtained in Fig. 3. The critical Reynolds number in the present work is smaller than the generally accepted value of 2300, probably due to the fact that the specific surface area of the resin is larger than the estimated value because of the pore structure in the resin particle. Since Eq. (7) Eq. (8) Eq. (9) Eq. (10) suggest that the Reynolds number increases if the specific surface area is enlarged, the critical Reynolds number shown in Figs. 3 and 4 may be somewhat smaller than the actual value in the present system.

In this paper, a comparison is made of the present work and previously reported works. HETPs are plotted against the product of the band velocity u_B and the square of the resin diameter d_p^2 in Fig. 5 with reported HETPs given by Spedding et al. [1], Park and Michaels [2], Kruglov et al. [3], a calculated HETP based on the data in the work reported by Urgell et al. [15], and HETPs obtained in our previous work [13]. It is seen in Fig. 5 that there is an empirical linear relation between $\ln H$ and $\ln(d_p^2 u_B)$ with a slope of 0.5 for HETPs obtained by

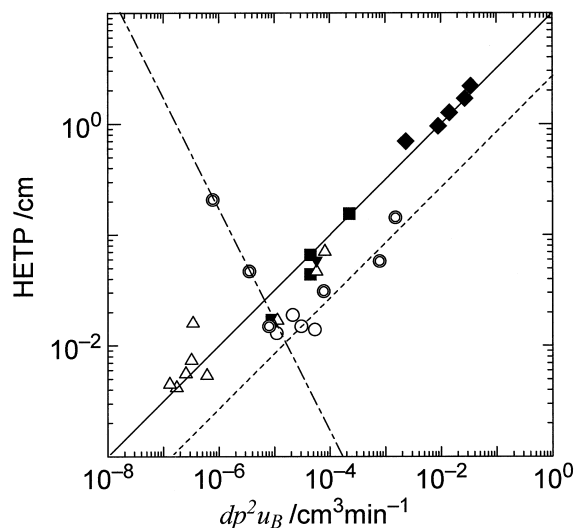


Fig. 5. Effect of band velocity and resin diameter on HETP. HETPs of gel-type resins: (■) Spedding et al. [1]; (△) Park and Michaels [2]; (▼) Urgell et al. [15]. HETPs of macroreticular resin: (◆) Kruglov et al. [3]. HETPs of microreticular resins: (⊙) present work; (○) our previous work [13]. Open symbols, single column operations; solid symbols, multi-column operations.

the authors of Refs. [1,2,15], using gel-type resin and by Kruglov et al. [3] using macroreticular resin. In the present work, $\ln H$ is also proportional to $\ln(d_p^2 u_B)$ with a slope of 0.5 in the high flow-rate region, however, HETP reduces with increase in the fluid velocity at very low flow-rates in the experiment. The following relation is given in the band velocity range above 0.23 cm/min (or superficial velocity > 0.49 cm/min).

$$H = ad_p(u_B)^{0.5} + b \quad (14)$$

As the performance of any separation process is characterized by the maximum separative power per unit volume [16], the optimal operating range for the flow-rate for this system lies in the band velocity above 0.23 cm/min (or superficial velocity > 0.49 cm/min). The maximum separative power per unit volume δU_m is defined as,

$$\delta U_m = \frac{(\epsilon^2 B)/4}{HA} \quad (15)$$

where B is the interstage mass flow-rate, and A the cross-sectional area of the column. In addition, since

Eq. (14) is valid only in the high-flow-rate region, the experimental data obtained in the low-flow-rate region where the band interface was tilted and/or channeled cannot be used for designing a process system. Fig. 5 also shows that the HETPs are improved to the dashed line by using the porous microreticular resin in comparison with the gel- and macroreticular-type resins shown by the straight line if the chromatographic operation is conducted in the high-flow-rate region.

Since the experimental conditions for the reported data shown in Fig. 5 are different, dimensionless parameters called the reduced plate height h and the reduced velocity v are introduced [17] in order to compare experimental data on the basis of some common yardstick. These are defined by following equations.

$$h = H/d_p \quad v = d_p u_B / D_m \quad (16)$$

where D_m is the diffusion coefficient of NH_4^+ ions in mobile phase ($1 \times 10^{-5} \text{ cm}^2/\text{s}$). The reduced plate height is plotted against the reduced velocity in Fig. 6. In the figure, the linear relation between $\ln h$ and $\ln v$ is confirmed for gel and macroreticular resin (straight line) and porous microreticular resin (dashed line) at the high reduced velocities. On the

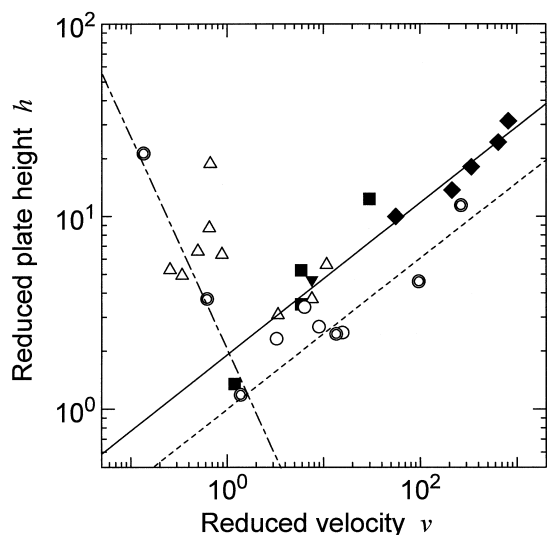


Fig. 6. Plots of reduced plate height vs. reduced velocity. Symbols are the same as those used in Fig. 5.

other hand, the reduced plate heights are enlarged in the case when the resin size or the band velocity are very small. The figure shows that the reduced plate height becomes large when the resin diameter is less than ca. $10 \mu\text{m}$ (triangles) and/or the band velocity is lower than $6.6 \times 10^{-2} \text{ cm}/\text{min}$ (double circles).

4. Conclusions

Nitrogen isotope separation was studied using porous microreticular cation-exchange resin for a wide range of flow-rates. It is found that a sharp band boundary is obtained and the proportional relation between HETP and square-root of the band velocity is confirmed in the turbulent flow regime. On the other hand, tilted and/or channeled band boundaries become large and HETP is inversely proportional to the flow-rate in the laminar flow regime. The use of porous microreticular resin improves HETP of isotope separation compared with gel- and macroreticular-type resins in a high-flow-rate region. It is also confirmed that HETP is proportional to the resin diameter and square-root of the band velocity at the high flow-rates, whereas it becomes large with decrease in fluid velocity at very low flow-rates due to the longitudinal mixing which is caused by tilting and/or channeling at the band boundary.

Acknowledgements

The authors wish to express their appreciation to Professor I. Okada and Dr. M. Nomura, Tokyo Institute of Technology, for kind advice and cooperation. The present work was financially supported by the Grant-in-Aid of Ministry of Education, Science and Culture of Japan (Project No. 07558280).

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