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S. Fujine[a]; K. Saito[a]; K. Shiba[a]
[a] Division of Nuclear Fuel Research, Japan Atomic Energy Research Institute Tokai, Ibaraki, Japan

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The Effects of Temperature and the Use of Macroreticular Resins in Lithium Isotope Separation by Displacement Chromatography

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S. FUJINE, K. SAITO, and K. SHIBA

DIVISION OF NUCLEAR FUEL RESEARCH
JAPAN ATOMIC ENERGY RESEARCH INSTITUTE
TOKAI, IBARAKI, JAPAN

Abstract

The effects of temperature and the use of macroreticular resins were studied in lithium isotope separation by an ion-exchange method. The isotope separation factors obtained decreased by increasing the temperature, and the factors for macroreticular resins were identical with those for the usual gel-type resins. However, the performance of isotope separation per unit band length in displacement chromatography was found to be improved by increasing the temperature and using macroreticular resins, because accelerating the interphase mass transfer caused the reduction of HETP (Height Equivalent to a Theoretical Plate).

INTRODUCTION

Lithium isotope separation by the ion-exchange method has been studied by a circuit of continuous displacement chromatography (*1–4*). The diffusion of Li^+ ions in resin particles was found to be the major resistance in the interphase isotope exchange reaction. We derived the following equation to estimate HETP (cm) (*3*) which is an important factor in determining the separation performance:

$$\mathrm{HETP} = \frac{u_B}{K_T a} + \frac{\varepsilon E}{\bar{u}} \tag{1}$$

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where u_B (cm/s) is the speed of moving bands, K_T (cm/s) is the overall mass transfer coefficients, a (cm^2/cm^3) is the area of interphase mass transfer per unit bed volume, ε is the void fraction of resin beds, E (cm^2/s) is the effective diffusivity of liquid mixing in the columns, and $\bar{u}$ (cm/s) is the superficial velocity of the displacement reagent. The first term on the right-hand side of Eq. (1) is due to the slow mass transfer, and the other term is due to liquid mixing. The overall capacity coefficient is expressed by

$$\frac{1}{K_T a} = \frac{1}{K_s a} + \frac{(q_0/\varepsilon C_0)}{K_L a} \tag{2}$$

where K_s (cm/s) is the mass transfer coefficient in the resin phase, K_L (cm/s) is the mass transfer coefficient in the liquid boundary layer surrounding the particles, q_0 (meq/mL) is the ion-exchange capacity, and C_0 (mol/L) is the concentration of the displacement reagent. The first term on the right-hand side of Eq. (2) is the more determinant, and the second term may be neglected for the present separation system. The capacity coefficient $K_s a$ (s^{-1}) in particles is expressed using Glueckauf's approximation (5):

$$K_s a = \frac{\bar{D}}{0.071 r_0^2} \tag{3}$$

where $\bar{D}$ (cm^2/s) is the diffusion coefficient in resin particles and r_0 (cm) is the radius of the particles. Therefore, the HETP decreases by increasing the diffusion coefficients and by decreasing the particle size.

The diffusion coefficients in particles can be increased by elevating the operational temperature and by reducing the cross-linkage of the resin matrix. Changing these factors, however, simultaneously decreases the isotope separation factor per single stage. The performance of isotope separation by displacement chromatography is determined by the combination of these opposite effects: increasing the mass transfer coefficients and reducing the isotope separation factors.

Small resin particles also increase the capacity coefficents, simultaneously increasing the flow resistance in the columns, which restricts the flow rate of the displacement reagents. A particle of macroreticular resins has a structure made of many fine grains and has a large specific surface area. The use of macroreticular resins is considered to be effective for increasing the capacity coefficients without increasing the flow resistance in the columns. Experiments of lithium isotope separation using macroreticular resins have been reported by Hagiwara (*6*). He emphasized that macroreticular Diaion PK240X20 resin, which does have a large void volume, gave a lithium isotope enrichment factor twice as large as gel-type resins. On the other hand, he indicated that the separation factors are decreased by increasing the void fraction in resin beds (*7*), using the equation of "effective separation factors" derived by Glueckauf (*8*). We consider these two ideas to be contradictory.

In order to study the effects of temperature and resin types, in the present report lithium isotope separation is carried out by a circuit of continuous displacement chromatography under operation conditions for which the isotope separation factors are newly obtained.

TEMPERATURE EFFECTS

The Influence of Temperature on the Isotope Separation Factor

In general, isotope separation factors have a tendency to decrease with temperature (*9*). As for lithium isotope separation by ion exchange, Lee and Begun have revealed the dehydration mechanism of lithium ions in resin particles (*10*):

$$^{6}\mathrm{Li}^{+}(\mathrm{H_2O})_4 + \overline{^{7}\mathrm{Li}^{+}(\mathrm{H_2O})_3} \rightleftharpoons {}^{7}\mathrm{Li}^{+}(\mathrm{H_2O})_4 + \overline{^{6}\mathrm{Li}^{+}(\mathrm{H_2O})_3}$$

where a bar represents the insides of resin particles. They expressed the isotope separation factor α by using Bigeleisen-Mayer's formula:

$$\alpha = 1 + \frac{\Delta M m}{24 M_h M_l}(u^2 n - \bar{u}^2 \bar{n}) \qquad (4)$$

where M_h is the mass of the heavier species, M_l is the mass of the lighter species, $\Delta M = M_h - M_l$, m is the mass of the surrounding atom (oxygen in this case), n is the number of hydration, and $u = hc\omega/kT$, where ω (cm^{-1}) is the symmetrical vibrational frequency and the other symbols have their usual meanings. The logarithm of α is considered to have linear relationship with $1/T^2$.

Frontal analysis (*11*) was applied to the present system of the gel-type, strong acid cation exchange resin, Diaion SK116, with particle diameter 100 μm and ion-exchange capacity 2.66 (meq/mL). The lithium isotope separation factors were obtained at 10, 20, and 40°C using 0.5 *M* $\mathrm{CH_3COOLi}$. The separation factors almost agree with Lee's data using LiCl (*12*), as shown in

Fig. 1. Referring to both sets of data, the experimental data may be expressed by

$$\alpha = 1.00046 \exp\left(\frac{220}{T^2}\right) \tag{5}$$

Experiments of Displacement Chromatography

Lithium isotope separation was carried out at several temperatures by a circuit of continuous displacement chromatography which was composed of 2 cm i.d. × 1 m Pyrex columns packed with Diaion SK116 resin (*2, 4*). The void fraction of the resin beds was 0.35. A displacement reagent of 0.5 *M* CH_3COONa solution was introduced at the top of a lithium adsorption band at a constant superficial velocity of 3 m/h, which corresponded to a moving band speed of 54 cm/h. The lithium bands moved with a constant band length, displacing the H-form resin. The experimental conditions are shown in Table 1.

The isotope concentration profiles in lithium bands, obtained at the steady state, give the linear lines on semilogarithmic ordinates as shown in Fig. 2. The slopes of the profiles are found to increase with temperature. The linear relation is explained by Fenske's equation of distillation theory (*1*):

$$S = \frac{\ln (R/R')}{\ln \alpha} \tag{6}$$

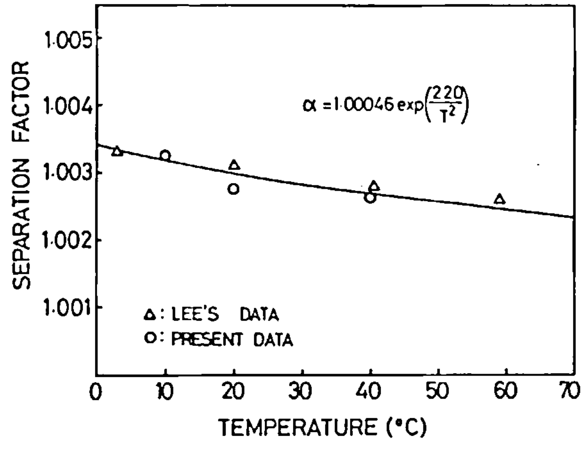

FIG. 1. Temperature dependence of lithium isotope separation factor.

TABLE 1

Experimental Conditions

Run	Temperature (°C)	Speed of moving band (cm/h)	Band length (cm)
1	13.	54.9	64.5
2	20.	54.0	60.2
3	38.	54.0	58.4

where S is the theoretical stage number in the band; R and R' are isotope ratios ($^6Li/^7Li$). Since the effluent volume in Fig. 2 can be converted to the length in the columns, HETP is obtained from the profiles using the isotope separation factors of Eq. (5). The value of HETP obtained decreases from 0.56 to 0.26 cm (which is 1/2.2 times) by increasing the operational temperature from 13 to 38°C, as shown in Fig. 3. That is, the performance of lithium isotope separation is improved by increasing the temperature because the acceleration of the ion-exchange reaction surpasses the decrease in the isotope separation factor.

Both boundaries of the lithium adsorption band become sharp with temperature, as shown in Fig. 4. Since countercurrent separation in total reflux operation is assumed in the columns of displacement chromatography,

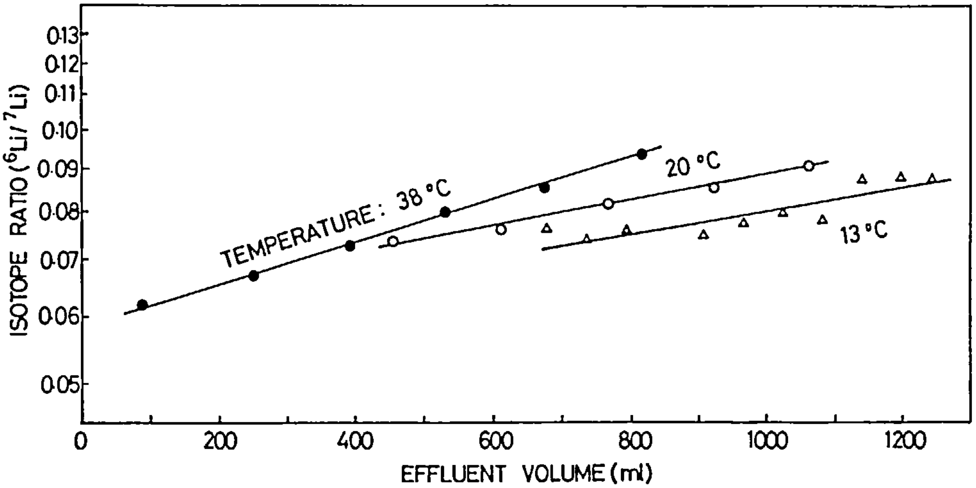

FIG. 2. Lithium isotope concentration profiles at steady state.

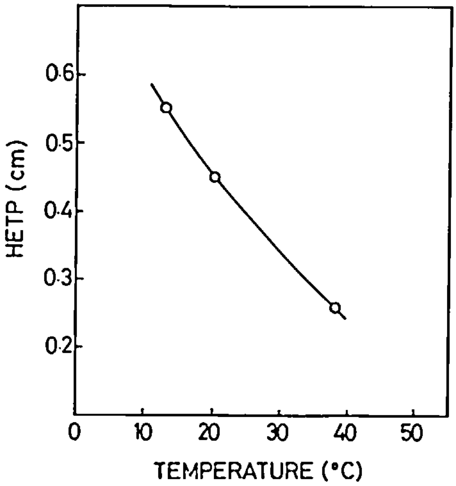

FIG. 3. Temperature dependence of HETP.

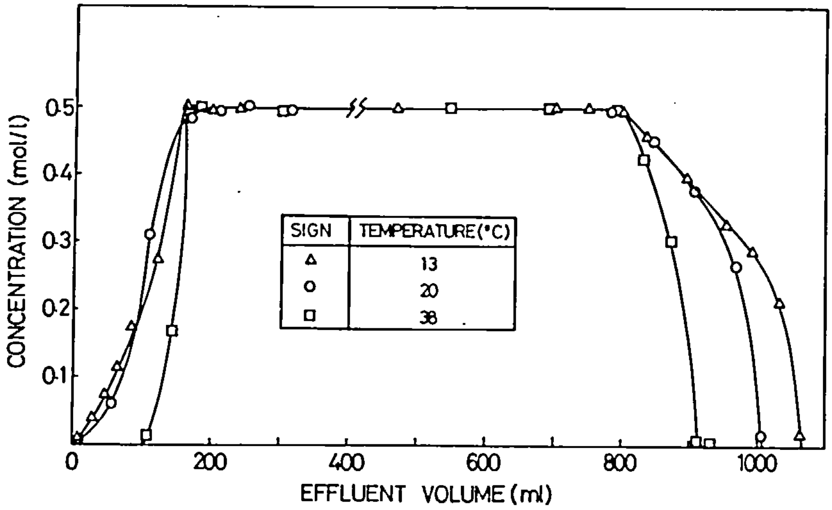

FIG. 4. Shapes of lithium adsorption bands.

the following equation holds for lithium concentration profiles at the ends of bands, on the assumption of resin-phase mass transfer control (*3*):

$$z = \frac{u_B}{K_s a} \int_{y_1}^{y_2} \frac{dy}{y^* - y} \tag{7}$$

where y represents the lithium mole fraction in the resin phase, y^* is the mole fraction at equilibrium with the mole fraction x in the liquid phase, and z (cm) is the distance between y_1 and y_2. The equilibrium constant

$$K_{\mathrm{Li}}^{\mathrm{Na}} = \frac{y}{1-y} \bigg/ \frac{x}{1-x}$$

has been found to be 2.57 (*2*). The operating line agrees with the diagonal of the y–x graph. The graphic integration from 0.05 to 0.95 of the lithium mole fraction gives the number of transfer unit (NTU):

$$(\mathrm{NTU})_{\mathrm{Li\text{-}Na}} = \int_{0.05}^{0.95} \frac{dy}{y^* - y} = 6.9 \tag{8}$$

The value of NTU may be approximated to be constant at the temperature of the present experiments because the standard enthalphy changes for the ion-exchange reactions are small. The capacity coefficients are obtained by Eq. (7) using the lithium concentration profiles at the rear boundary in Fig. 4. Figure 5 shows the temperature dependence of the capacity coefficients obtained. The coefficients are found to increase by 2.2 times by increasing the temperature from 13 to 38°C. The extent is similar to that of the HETP of lithium isotope separation.

DISCUSSION

We experimentally obtained the diffusion coefficients of Li^+ ions in the resin particles of Diaion SK116 in order to know whether improvement in the performance of lithium isotope separation was expected by further elevation of temperature over 40°C. Figure 6 shows the temperature dependence of Li^+ self-diffusion coefficients obtained by the batch method (*13*) on the assumption of resin-phase diffusion control. The figure also shows the diffusion coefficients which are obtained from the data of HETP

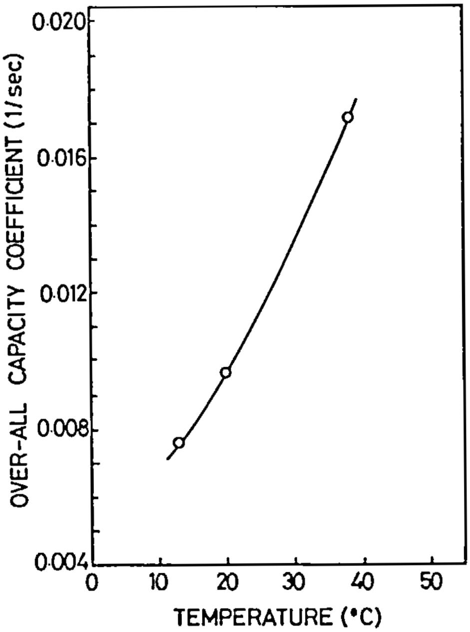

FIG. 5. Temperature dependence of overall capacity coefficient.

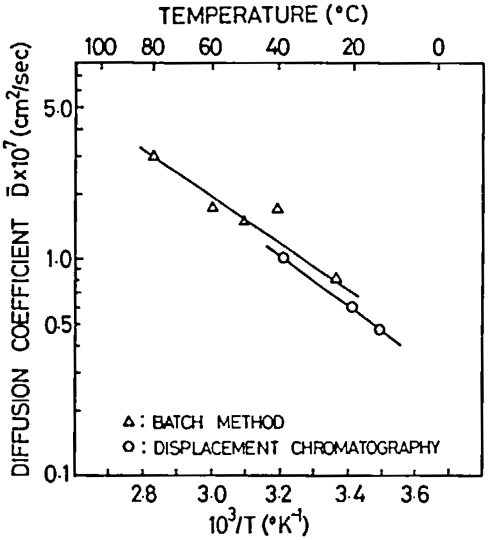

FIG. 6. Temperature dependence of diffusion coefficients in resin particles.

for lithium isotope separation by displacement chromatography, using the following equation to estimate the value of HETP (*3*):

$$\mathrm{HETP} = \left(\frac{C_0}{q_0 + \varepsilon C_0}\right)\frac{0.071 r_0^2}{\bar{D}}\bar{u} + \frac{\varepsilon E}{\bar{u}} \tag{9}$$

where the term due to slow diffusion in the boundary layer surrounding the particles are eliminated. The effective diffusivity representing liquid mixing in the column has been found to be 0.031 cm^2/s, which corresponds to $\varepsilon E/\bar{u} = 0.13$ cm (*3*). Agreement among these diffusion coefficients is noticed in Fig. 6. The activation energy is found to be 5.4 kcal/mol. The diffusion coefficients may be expressed by

$$\bar{D} = 6.0 \times 10^{-4} \exp\left(-\frac{2704}{T}\right) \tag{10}$$

The ratio of the isotope ratios at positions which are a unit length apart is considered to be a suitable index representing the performance of separation by displacement chromatography. According to Eq. (6), the index is rewritten as

$$R/R' = \alpha^S \tag{11}$$

where S (cm^{-1}) represents the number of theoretical stages per unit band length and equals the reciprocal of HETP. The temperature dependence of the index is obtained by substituting Eqs. (5), (9), and (10) into Eq. (11), as shown in Fig. 7 for the present experiments. The index is found to increase with temperature to the general critical limit of 120°C for strong acid cation exchange resins, in spite of the decrease in the isotope separation factor per stage.

THE USE OF MACRORETICULAR RESINS

Lithium Isotope Separation Factor

Lithium isotope separation factors were obtained using a macroreticular resin, Diaion AHPK-16S, of sulfonated cation exchange resins. The degree of cross-linkage and particle size of this resin are the same as those of Diaion

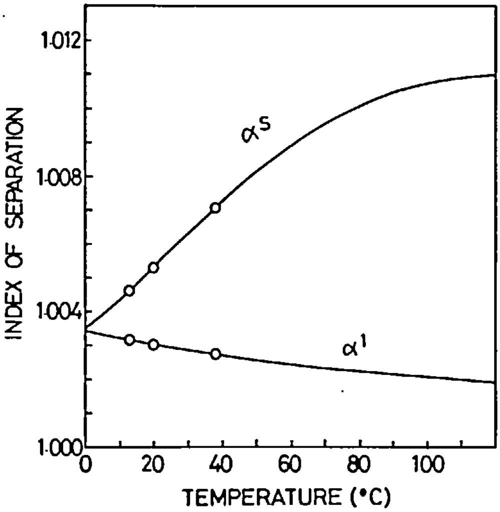

FIG. 7. The magnitude of separation per unit band length affected by temperature.

SK116. The specific surface area is 10 m^2/g, which corresponds to that of fine gel-type resins of about 0.8 μm in diameter. The pore volume in the particles is 0.5 mL/g and the mean pore radius is 1095 Å. The ion exchange capacity is 1.27 meq/mL, about half of that for Diaion SK116.

The isotope separation factors obtained are 1.0031 for 0.48 *M* CH_3COOLi at 20°C and 1.0028 for 0.49 *M* CH_3COOLi at 40°C. These values for the macroreticular resin are almost equal to those for gel-type resins. Hagiwara reported that lithium isotope enrichment factors for macroreticular resins were found to be twice the value of gel-type resins (*6*). We consider that the increase in specific surface area of resins does not have a significant effect on the isotope separation factors, because the dehydration of lithium ions by the matrix in resin particles is mainly responsible for isotope separation.

Experiments of Displacement Chromatography

Lithium isotope separation was carried out using the macroreticular resin Diaion AHPK-16S by a circuit of continuous displacement chromatography. Figure 8 shows the concentration profiles at 72.2 h when steady state has

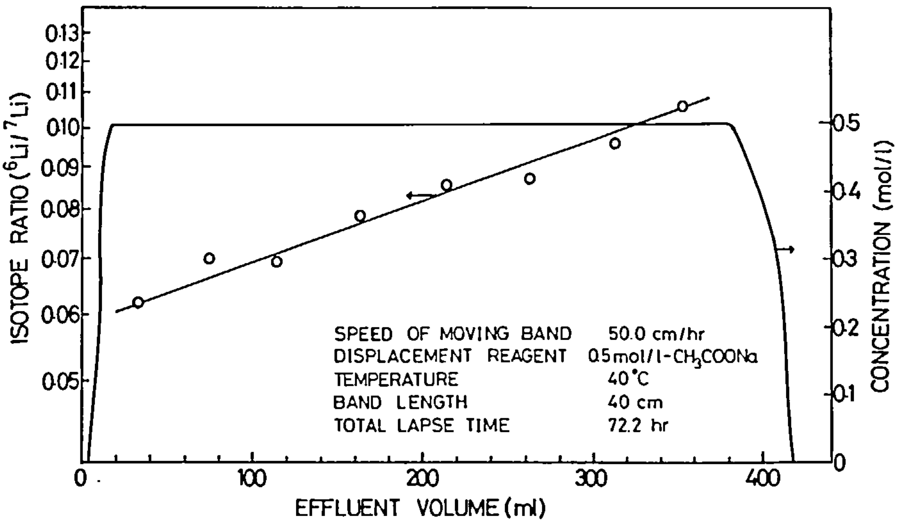

FIG. 8. Concentration profiles at steady state.

been attained. A displacement reagent of 0.5 M CH_3COONa was fed at a constant superficial velocity of 1.57 m/h, and a lithium adsorption band of 40 cm length moved at the speed of 50 cm/h in the columns. The void fraction of the resin bed was 0.58. The operational temperature was 40°C. Another run for the resin was carried out at a moving band speed of 86.8 cm/h which corresponded to a superficial velocity of 2.72 m/h. These isotope concentration profiles for the macroreticular resin are shown in Fig. 9 with the profile at 38°C for the gel-type resin, Diaion SK116. The slopes of the profiles for the macroreticular resin are found to be larger than that for the gel-type resin at the speed of moving band, 54 cm/h. This reveals that the isotope separation per unit band length is improved by the use of macroreticular resins. Since the isotope separation factors for both resins are identical, the improvement is considered to be caused by the increment of capacity coefficients by increasing the interphase mass transfer area. Figure 10 shows HETP versus the speed of the moving bands. For the macroreticular resin at 40°C, the relation may be expressed by

$$\mathrm{HETP} = 7.56u_B + 0.037 \qquad (12)$$

where the dimension of u_B is cm/s. The values of HETP obtained for the gel-

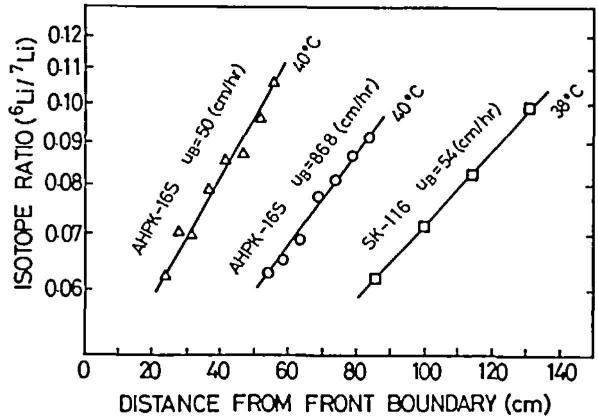

FIG. 9. Comparison of lithium isotope concentration profiles for macroreticular and gel-type resins.

type resin are also shown in Fig. 10. The data for the gel-type resin at 20°C are expressed by

$$\text{HETP} = 17.28u_B + 0.126 \tag{13}$$

which has been reported (*3*).

Blanco et al. separated lithium isotopes by a continuous countercurrent fluidized bed of ion-exchange resins (*14*) which required a 400-cm length of the bed to increase the isotope ratio (^{6}Li/^{7}Li) from 0.07 to 0.09. A band length of only about 15 cm, however, is good enough for the same concentration change in the present experiments where the band moves at a

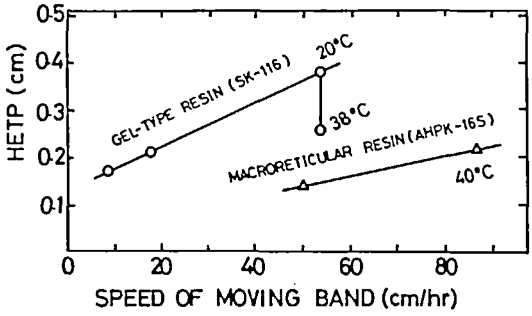

FIG. 10. Relations between HETP and speed of moving band.

speed of 50 cm/h at 40°C in the fixed beds packed with the macroreticular resin. Fluidized beds are considered to cause a stronger liquid mixing than fixed beds. Lithium isotope separation factors are so small that the liquid mixing in the beds should be minimized and HETP should be maintained as small as possible.

DISCUSSION

The dependence of HETP on the speed of moving bands for lithium isotope separation is considered to be analogous to the dependence of HTU (Height of a Transfer Unit = u_B/K_Ta cm) on the speed of moving boundaries for the separation of lithium ions from other element. In order to know whether small values of HETP were also expected for the faster movement of bands in columns packed with the macroreticular resin, we obtained breakthrough curves of Li^+ ions eluted from H-form resin beds of 1-m length using 1 *M* LiOH solution at 20°C, and obtained HTU by Eq. (7) using the value of NTU (*15*):

$$(\mathrm{NTU})_{\mathrm{Li\text{-}H}} = \int_{0.05}^{0.95} \frac{dy}{y^* - y} = 3.0 \tag{14}$$

The values of HTU obtained increase with the speed of moving boundaries for the gel-type resin. However, this increasing tendency is not obvious for the macroreticular resin and the HTU is maintained at small values, as shown in Fig. 11. The overall capacity coefficients, obtained by Eq. (7) on the basis of the concentration in resin particles, are found to increase with the speed of the moving boundaries for both resins. This phenomenon is caused by the decrease of the resistance for diffusion in the liquid boundary layer surrounding the particles because the flow in columns increases with the speed of moving boundaries. Yamamoto has reported the following relation between HTU and Reynolds number ($\mathrm{Re} = \rho \bar{u} d_p/\mu$) for ion-exchange operation (*16*);

$$\frac{1}{\mathrm{HTU}} \propto \mathrm{Re}^{-0.55} \tag{15}$$

where ρ (g/cm^3) is the density of the fluid, μ (g/cm·s) is the viscosity, and d_p

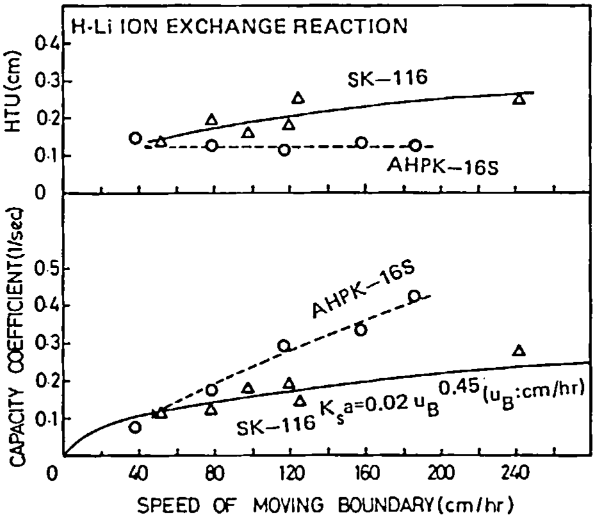

FIG. 11. HTU and capacity coefficient as functions of speed of moving boundaries.

(cm) $= 2r_0$. The superficial velocity in the column is expressed, using the speed of the moving bands, by

$$\bar{u} = \left(\frac{q_0}{C_0} + \varepsilon\right) u_B \tag{16}$$

Therefore, Eq. (15) may be rewritten, using the relation of HTU $= u_B/K_T a$, by

$$K_T a \propto u_B^{0.45} \tag{17}$$

This relation agrees with the data obtained for the gel-type resin, as shown in Fig. 11. As for the macroreticular resin, however, the flow rate is found to have more significant effects on the interphase mass transfer. We consider that a part of the liquid flow passes through macropores in the particles, and that the fraction of the passing flow decreases by decreasing the flow rate beacuse the overall capacity coefficients are found to become equal for both resins at the slow speed of the moving boundary.

Lithium adsorption bands of displacement chromatography may be regarded as countercurrent separators in total reflux operation, and the following fundamental equation is derived (*1*):

$$\frac{\partial N}{\partial \tau} = \frac{\partial^2 N}{\partial S^2} - (\alpha - 1)\frac{\partial}{\partial S}\{N(1 - N)\} \qquad (18)$$

where N represents the isotope mole fraction and τ is the dimensionless time expressed by

$$\tau = \frac{L'}{H_0} t = \frac{q_0}{(q_0 + \varepsilon C_0)} \frac{u_B}{(\mathrm{HETP})} t \qquad (19)$$

L' (mol/s) represents the theoretical interstage flow rate expressed by

$$L' = q_0 u_B \qquad (20)$$

for unit cross-sectional area of the columns, and H_0 (mol) is the holdup per stage. Macroreticular resins have a disadvantage in the interstage flow rate because the ion-exchange capacities of the resins are smaller than those of gel-type resins. However, the disadvantage may be avoided by increasing the speed of the moving bands. Increasing the speed of the moving bands while keeping HETP small means that the lithium band passes through the more theoretical stages per unit time. That is, "the average process time per stage" h' (s), defines by Cohen (*17*) as

$$h' = H_0/2L' \qquad (21)$$

becomes smaller for macroreticular resins. Equation (19) gives a larger dimensionless time τ, and the isotope separation progresses more quickly in the bands for the separation system with a smaller average process time per stage. Thus the performance of isotope separation is improved for macroreticular resins.

CONCLUSION

The effects of temperature and the use of macroreticular resins were studied in lithium isotope separation by the ion-exchange method. The following conclusions were reached.

(1) The elevation of operational temperature reduces the isotope separation factors. However, the performance of lithium isotope separation by displacement chromatography is improved by increasing the temperature because the acceleration of the ion-exchange reaction surpasses the decrease in the isotope separation factor. The performance is expected to be improved with increasing temperature to the critical limit of the resins.

(2) The macroreticular resin AHPK-16S gives isotope separation factors almost equal to those for gel-type resins. The performance of lithium isotope separation per unit band length is improved because HETP becomes smaller by increasing the interphase mass transfer area. Increasing the speed of the moving bands while keeping HETP small means that the lithium band passes through more theoretical stages per unit time, and isotope separation progresses more quickly.

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