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Analysis of the Elution Curve in Eluting Lutetium from Cation-Exchanger with α-Hydroxyisobutyric Acid

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The elution behavior of lutetium from a cation-exchange column with α-hydroxyisobutyric acid solution (pH 3.77) was studied as a function of column distribution ratio of lutetium, flow rate, temperature and amount of lutetium. The elution curve fitted the normal distribution when the flow rate was smaller than 40 cm hr^{-1} for 0.14 M of the eluant, 60 cm h^{-1} for 0.12 M and 120 cm h^{-1} for 0.10 M. However, the normal distribution and constancy of the peak position could not be maintained when the amount of lutetium exceeded 200 μg cm^{-2}. Within the range 15—35 °C, the peak position appeared late and the elution curve became sharper with temperature rise, but the diffusion coefficients remained constant. The value of the height equivalent to the theoretical plate was determined from the position and width of the elution peak which varied as a function of the flow rate. The diffusion coefficients of lutetium ions in the ion-exchange resin and the solution were calculated to be 2.6×10^{-7}—$6.4\times10^{-9}\,\lambda''$ cm^{2}s^{-1} and $4.2\times10^{-5}\,\lambda''$ cm^2 s^{-1}, respectively, according to Glueckauf's theoretical equation, where λ'' is the column distribution ratio of lutetium ions. The experimental results make it possible to construct an elution curve for any column distribution ratio of lutetium in the range 2—20, temperature and flow rate.

In the cation-exchange separation of trace amounts of rare earths, α-hydroxyisobutyric acid has been used as the most prominent eluant. However, there are few reports on quantitative discussion of the elution behavior in connection with such factors as compositions of the eluant, operating temperatures, amounts of rare earths, *etc.* Only Seyb,[1] Massart and Hoste[2] have reported that yttrium and terbium can be separated successfully only by using eluant solutions containing sufficient amounts of undissociated hydroxy acid, and that the operating temperature and the amount of lutetium absorbed on the resin bed affect the appearance and shape of the elution peak. Although the flow rate of the eluant is an important factor influencing the separation, no one has ever discussed quantitatively the effect of flow rate on elution behavior of rare earths.

According to Glueckauf,[3] the elution curve can be expressed as follows with the assumption that the ion-exchange reaction is reversible:

$$C_i(V) = C_{i\max}\exp\left[-\frac{N(V_i-V)^2}{2V_iV}\right] \tag{1}$$

where C_i=concentration of species i in the effluent
N=plate number
V=effluent volume—dead volume of the column
V_i=effluent volume at which the concentration of the given ion reaches its maximum—dead volume of the column.

The shape of the elution curve apparently depends on V_i and N obtained by dividing the bed length (L) by the height equivalent to the theoretical plate (HETP). The value of HETP can be calculated by the theoretical formula:[3]

$$\mathrm{HETP} = 1.64\,r_0 + \frac{\lambda_i''0.14r_0^2u}{(\lambda_i''+\beta)^2\bar{D}} + \left(\frac{\lambda_i''}{\lambda_i''+\beta}\right)^2\frac{0.266\,r_0^2u}{D(1+70\,r_0u)} + \frac{D\beta\sqrt{2}}{u} \tag{2}$$

where r_0=radius of spherical ion-exchange resin particle
λ_i''=column distribution ratio of species i
$=\dfrac{\text{amount of species } i \text{ per ml of the resin bed}}{\text{amount of species } i \text{ per ml of the solution}}$
β=fractional void volume of the resin bed
u=linear flow rate of the eluant
$\bar{D}$=interdiffusion coefficient in the ion-exchange resin
D=diffusion coefficient in the solution

Of the right hand terms of the equation, the first is due to finite particle size, the second to slow particle diffusion, the third to slow film diffusion, and the last to longitudinal diffusion. This equation indicates that the HETP varies with the flow rate of the eluant. If Eq. (2) is applicable to the elution of lutetium with α-hydroxyisobutyric acid, and the diffusion coefficients are known, the equation enables us, in combination with Eq. (1), to construct an elution curve for any flow rate at a given column distribution ratio.

This paper deals with the effect of the flow rate as the main subject in the study of the elution behavior of lutetium from cation-exchange resin bed with α-hydroxyisobutyric acid solution having pH 3.77, the most suitable for the separation of thulium and lutetium at a lutetium distribution coefficient of around 10 ml·g^{-1}. The temperature dependence of the diffusion coefficients as well as the column distribution ratio and the variation of elution curve with the amount of lutetium were also studied.

The elution curves obtained under various conditions were analyzed to get HETP, and the diffusion coefficients $\bar{D}$ and D were determined as a function of λ'' so as to satisfy Eq. (2). The results enabled us to construct an elution curve under arbitrary conditions.

Experimental

Reagent and Apparatus. *Ion-exchange Resin*: Cation-exchange resin (Diaion SK-1, 100~200 mesh) was digested with a mixture of 30% hydrogen peroxide, ethylendiaminetetraacetic acid and ammonium hydroxide, and washed with distilled water. This ion-exchange resin was successively treated in a glass column with a large excess of 3 M hydrochloric acid and 3 M ammonium chloride. After being washed with distilled water, the resin was suspended in distilled water in a large glass column to collect particles of uniform size. Over 95% of the particles thus obtained had a diameter between 100~150 μm in 0.10 M α-hydroxyisobutyric acid solution, as confirmed by microscopic examination. The resin was stored in distilled water.

Column: A glass column of 0.8 cm in diameter and 25.0 cm in length with a water jacket was used. Water was circulated through the jacket to keep the column temperature at 15.0± 0.1 °C unless otherwise stated.

Eluant: α-Hydroxyisobutyric acid (HB), supplied by Wako Chem. Co., was dissolved in redistilled water to give a 2.5 M solution, and in redistilled water and concentrated ammonia solution to give a 2.5 M solution having pH 6.97. The acid solution (2.5 M) was mixed with a salt solution (2.5 M NH_4B) in a volume ratio of 3 : 2. Finally, eluants were prepared simply by diluting this mixed solution with redistilled water.

Lutetium Tracer: Lutetium-177 was produced by neutron irradiation of "spec pure" lutetium oxide, which had been spectrographically guaranteed by Johnson Matthey Co., in the JRR-2 reactor with a thermal neutron flux of 3×10^{13}n $cm^{-2}s^{-1}$. The irradiated oxide (5 mg Lu_2O_3) was dissolved in concentrated hydrochloric acid, dried under an infrared lamp and finally dissolved in 50 ml of 0.1 M hydrochloric acid.

Procedure. A resin slurry was poured into the column to make a resin bed of 21.9 cm long. Before each experiment, the bed was washed with eluant until the pH of the effluent became the same as that of the eluant. The lutetium tracer solution was introduced into the column. The column was then washed successively with 2 ml of distilled water, 0.5 ml of 0.5 M ammonium chloride solution and 1.5 ml of distilled water. Lutetium absorbed was eluted with the α-hydroxyisobutyric acid solution. The effluent from the column was passed through a thin polyethylene tube connected to the column and wound into a spiral to record its radioactivity counting rate continuously with an end-window GM counter. The flow rate was controlled by varying the height of the exit of the tube. One drop was taken from every one ml of the effluent onto a glass plate and evaporated to dryness with an infrared lamp. The radioactivity was counted with a GM counter to make an elution curve. The fractional void volume of the resin bed was determined with $^{131}I^-$ by the eqution

$$\beta = \frac{V_{^{131}I^-}}{V_b} \tag{3}$$

where V_b=bed volume of the column and $V_{^{131}I^-}$=effluent volume at which the first appearance of $^{131}I^-$ is confirmed in the effluent solution—dead volume of the column. The column distribution ratio of lutetium was determined from the peak position of lutetium activity by the equation

$$\frac{V_i}{V_b} = \lambda_i'' + \beta \tag{4}$$

Results and Discussion

Effect of Flow Rate on Elution Curve. Elution curves are shown in Figs. 1, 2 and 3 as a function of the flow rate and concentration of the eluant. At the elution with 0.10 M solution with a flow rate up to 120 cm h^{-1}, elution curves were symmetrical within 5% with respect to the vertical line passing the maximum of the peak. However, as the eluant concentration increases, the maximum flow rate at which a symmetrical elution curve is obtained, becomes small, *i.e.*, up to 60 cm h^{-1} for 0.12 M and 40 cm h^{-1} for 0.14 M (Figs. 2 and 3). Variations of the widths at 1/2, 1/10, $1/10^2$, and $1/10^3$ peak height of the elution curves are shown in Fig. 4 as a function of the flow rate for 0.12 M eluant. Apparently a linear relation holds between the flow rate and the width of the elution peak within the symmetrical flow rate region (0~60 cm h^{-1}). This differs from the elution with citric acid,[4] where the width of the elution peak is

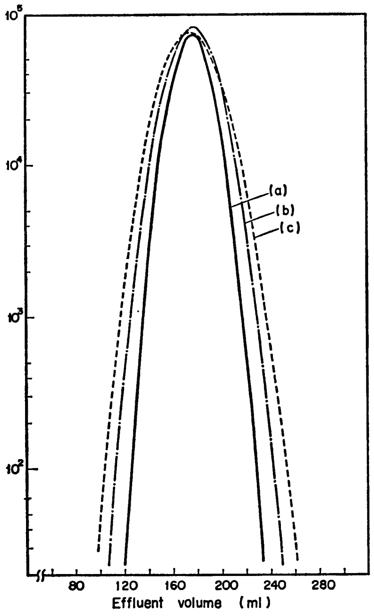

Fig. 1. Effect of the flow rate on the elution curve at the eluant concentration of 0.10 M.
(a): 21.9 cm h^{-1}, (b): 69.0 cm h^{-1}, (c): 116 cm h^{-1}.

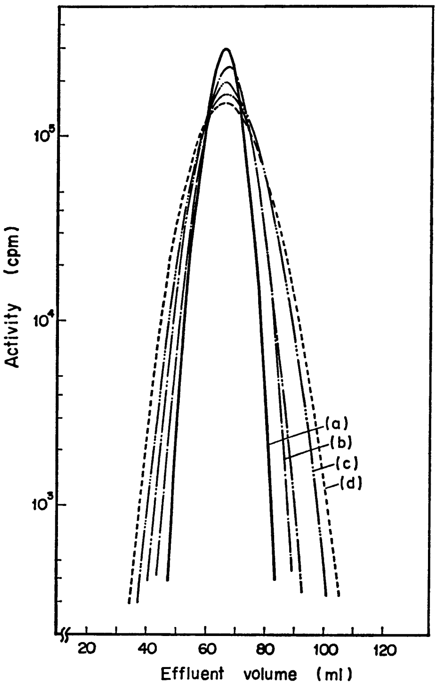

Fig. 2. Effect of the flow rate on the elution curve at the eluant concentration of 0.12 M.
(a): 16.8 cm h^{-1}, (b): 34.8 cm h^{-1}, (c): 53.1 cm h^{-1}, (d): 90.5 cm h^{-1}, (e): 118 cm h^{-1}.

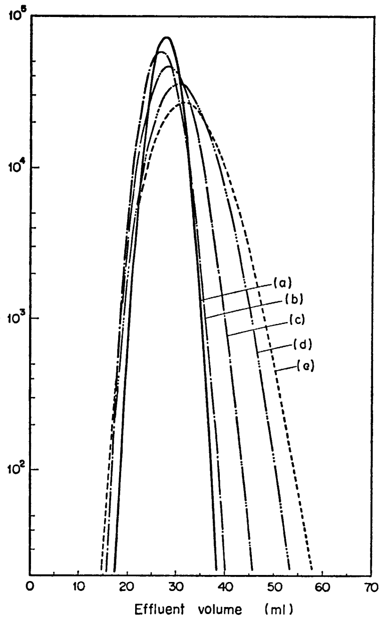

Fig. 3. Effect of the flow rate on the elution curve at the eluant concentration of 0.14 M.
(a): 15.9 cm h^{-1}, (b): 29.8 cm h^{-1}, (c): 47.2 cm h^{-1}, (d): 83.6 cm h^{-1}, (e): 109 cm h^{-1}.

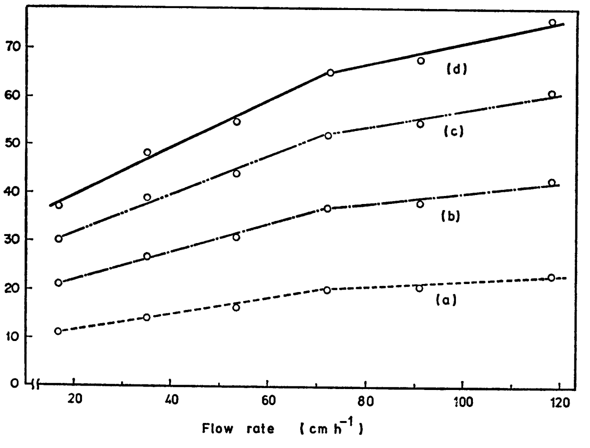

Fig. 4. Relation between the peak widths and the flow rate at the eluant concentration of 0.12 M.
(a): peak width at 1/2 peak height, (b): peak width at 1/10 peak height, (c): peak width at $1/10^2$ peak height, (d): peak width at $1/10^3$ peak height.

nearly independent of the flow rate below 30 cm h^{-1}. Ratios of the widths at 1/2, $1/10^2$ and $1/10^3$ peak height to that at 1/10 peak height do not vary with the flow rate and consist of those of the normal distribution curve.

For the symmetrical flow rate region in which the ion-exchange is considered to proceed reversibly, HETP can be calculated from the elution curve by the simplified equation[3])

$$\mathrm{HETP} = \frac{L}{16}\left(\frac{\Delta V_i}{V_i}\right)^2 \tag{5}$$

where the bandwidth ΔV_i of species i is defined as the number of solution-volume units in the effluent between the intercepts of the tangents to the front and rear flanks of the peak with the abscissa.[3]) The values of HETP calculated from Eq. (5) show linear increase with the flow rate (Fig. 5). The increase in the concentration of the eluant, or the decrease in the distribution coefficient makes the slope steeper. However, the change of the slope can not be explained only by the variation of the column distribution ratio λ_i'' in Eq. (2). The variation of the diffusion coefficients with the eluant concentration should be taken into consideration.

The diffusion coefficients $\overline{D}$ and D, which satisfy the relation of Eq. (2), were calculated by means of Eq. (2) and experimental values of $r_0=1.31\times10^{-2}$ cm, $\beta=0.33$, and $\lambda_i''=17.3$ for 0.1 M α-hydroxyisobutyric acid solution, 6.26 for 0.12 M and 2.29 for 0.14 M. The results are shown in Fig. 6. The interdiffusion coefficient in the ion-exhcanger $\overline{D}$ increases with the concentration of the eluant, contrary to the view that the diffusion coefficient decreases with increase of salt concentration. The diffusion coefficient in solution D decreased as the concentration of the eluant increases.

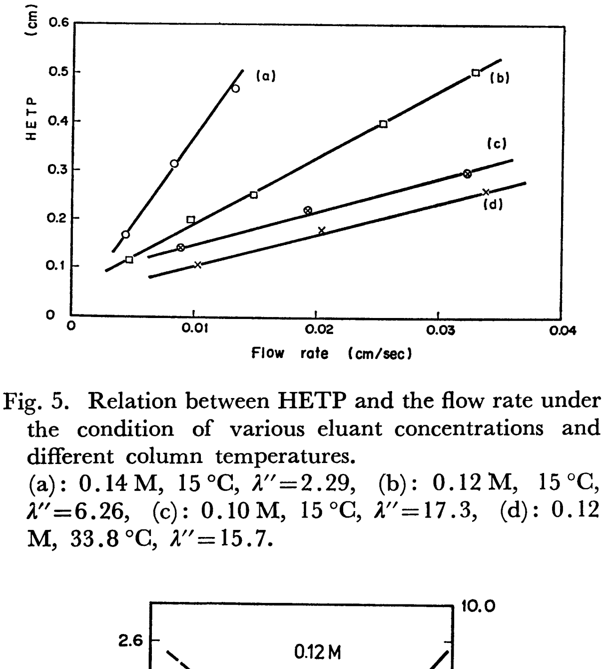

Fig. 5. Relation between HETP and the flow rate under the condition of various eluant concentrations and different column temperatures.
(a): 0.14 M, 15 °C, $\lambda''=2.29$, (b): 0.12 M, 15 °C, $\lambda''=6.26$, (c): 0.10 M, 15 °C, $\lambda''=17.3$, (d): 0.12 M, 33.8 °C, $\lambda''=15.7$.

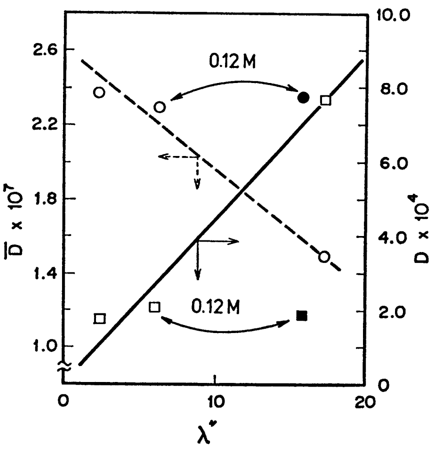

Fig. 6. Relations between the column distribution ratio and the diffusion coefficients $\overline{D}$ and D.
○: $\overline{D}$ at 15 °C, □: D at 15°C, ●: $\overline{D}$ at 33.8 °C, ■: D at 33.8 °C.

Brücher and Szarvas[5] recognized a similar phenomenon, *viz.*, the interdiffusion coefficients of cerium and promethium ions in the ion-exchanger increase with the concentration of ammonium lactate. They explained the phenomenon to be due to the decrease of the charge from 3 to a value around 2 of the rare earth ions diffusing in the resin phase owing to the formation of lactate complex above a certain ammonium lactate concentration. By applying their explanation to the present work, the increase of $\bar{D}$ with the eluant concentration can be connected to the increase in the contribution of LuB^{2+} ions to the ion-exchange reaction, where B is α-hydroxyisobutyrate ion. The assumption of the absorption of lutetium as LuB^{2+} ions is consistent with the view of Holm[6] and Powell.[7] However, the contribution of LuB^{2+} ions is thought to be smaller than that of Lu^{3+} ions, since the interdiffusion coefficient obtained in this work is almost consistent with that of Lu^{3+} ions.[8]

The linear relationships between $\bar{D}$ and D, and λ_1'' in Fig. 7 can be expressed as $\bar{D}=2.6\times10^{-7}$—$6.4\times10^{-9}\ \lambda_1''$ and $D=4.2\times10^{-5}\ \lambda_1''$, respectively. Consequently, in the case of separating lutetium with the eluant of pH 3.77, HETP at an arbitrary column distribution ratio and a flow rate can be calculated by substituting the above expressions for $\bar{D}$ and D into Eq. (2).

Effect of Temperature on Elution Curve. The elution curves of lutetium (Fig. 7) were obtained when the operating temperature varied within the range 15—35 °C. The peak position or the column distribution ratio varies greatly with temperature. There is a linear relationship between the column distribution ratio and the reciprocal of absolute temperature (Fig. 8). A similar linear relation was observed by Seyb[1] for terbium and yttrium except that his temperature dependence is rather small.

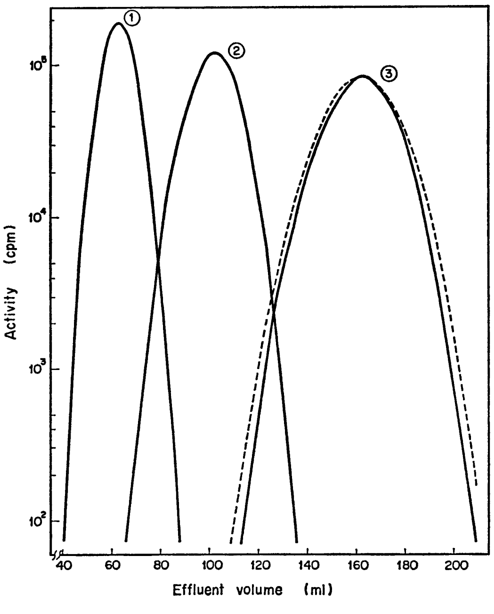

Fig. 7. Variation of the elution curve with column temperature at the eluant concentration of 0.12 M.
①: 15 °C, 33.6 cm h^{-1}, ②: 25 °C, 44.4 cm h^{-1}, ③: 34.8 °C, 50.1 cm h^{-1}.
The dotted line represents the calculated elution curve obtained at the column temperature of 15 °C by changing the eluant concentration so as to fit the peak position to that of case ③.

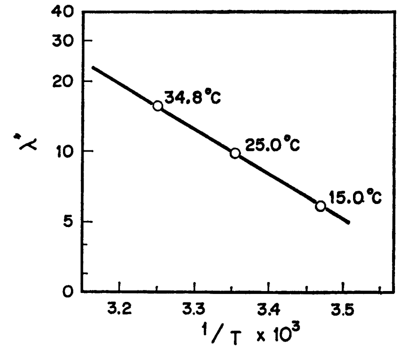

Fig. 8. Relation between the column distribution ratio and the reciprocal of absolute temperature (T).

From a direct comparision of the elution curves in Fig. 7, it is not clear whether a sharper elution peak can be obtained or not with temperature rise, since the peak position of lutetium is not kept constant. The effect of temperature on the shape of the elution peak can be analyzed by taking the variation of the diffusion coefficients due to the rise of temperature into consideration.

The values of HETP and the diffusion coefficients $\bar{D}$ and D at 33.8 °C were calculated in the same way as described above. The results are plotted in Figs. 5 and 6, respectively. The $\bar{D}$ and D values are equal to those obtained for the same concentration of the eluant at the operating temperature 15 °C (Fig. 6). The decrease of HETP with the increase of the column distribution ratio due to the rise of the operating temperature from 15 °C to 33.8 °C (compare b and d

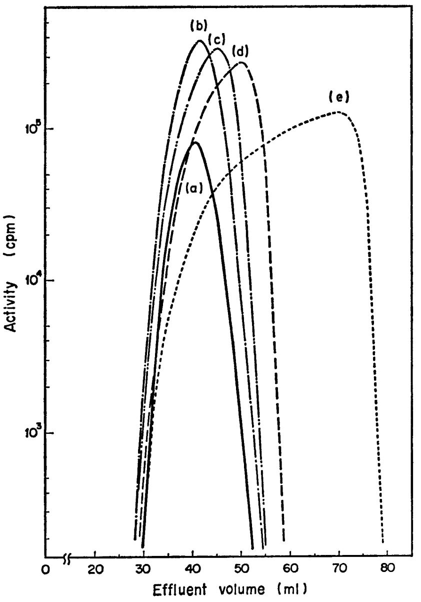

Fig. 9. Variation of the elution curve with the amounts of lutetium.
(a) 16 μg cm^{-2}, (b) 200 μg cm^{-2}, (c) 1.00 mg cm^{-2}, (d) 2.00 mg cm^{-2}, (e) 10.0 mg cm^{-2}.

in Fig. 5) exceeds the decrease of HETP by the increase of the column distribution ratio due to the decrease of the concentration of the eluant from 0.12 M to 0.10 M at 15 °C (compare b and c in Fig. 5), since the decrease of the concentration of the eluant results in the decrease of $\bar{D}$ and the increase of D as well as the increase of the column distribution ratio.

When the concentration of the eluant at 15 °C is selected so as to give the same column distribution ratio as obtained with 0.12 M of the eluant at 34.8 °C, the calculated elution curve of lutetium becomes as shown by the dotted line in Fig. 7. Obviously a sharper elution curve can be obtained by raising the operating temperature from 15 °C to 34.8 °C.

Effect of Lutetium Amount on Elution Curve. The shape of the elution curve of lutetium varies as shown in Fig. 9 as the amount of lutetium increases. The peak positions of the elution curves are the same in a deviation of 5% up to 200 μg cm^{-2} of lutetium. The result differs from that of Massart and Hoste.[2] Over 200 μg cm^{-2}, however, the symmetric elution curve is deformed rapidly with the increase of lutetium amount, simultaneously with the delay of the appearance of the position of the elution curve.

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