CONTINUOUS SEPARATION USING AN ANNULAR CHROMATOGRAPH WITH NON-ISOCRATIC ELUTION

YOUICHI TAKAHASHI AND SHIGEO GOTO
Department of Chemical Engineering, Nagoya University, Nagoya 464-01

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Introduction

A continuous chromatographic system has been developed for preparative separations. Moving chromatographic beds and simulated moving beds are mostly restricted to two-component separation[1]. On the other hand, a continuous rotating chromatograph first proposed by Martin[4] can be used for multi-component separation.

In our previous papers[2,6], a continuous rotating annular chromatograph (abbreviated as CRAC) with a rotating feed nozzle and product collectors was proposed. In this paper, the non-isocratic elution with two nozzles is applied to the CRAC to eluate strongly adsorbed components earlier. One nozzle is used to flow feed stream and the other nozzle is used to flow the second eluent.

The principle of the CRAC with the non-isocratic elution is shown schematically in **Fig. 1.** Feed is introduced at one rotating point and eluent fluid (Eluent 1) is supplied everywhere else. The products are collected by collectors which rotate at the same angular speed as the feed point. As elution proceeds, solutes progress down the annulus, giving the appearance of helices as the feed point rotates. If the adsorption force of the last eluated component is much stronger than that of the other two components, this component may be eluated at a greater angle than 360 degree and will be overlapped with the other two components as in the dotted lines of Fig. 1. To weaken the adsorption force of the last component, another eluent fluid (Eluent 2) is introduced from the second nozzle. Then, the last component can be eluated earlier and may be separated from the other two components.

Three kinds of amino acids—glutamic acid, glycine and valine—were chosen as multicomponents. Adsorption isotherms and kinetic parameters were determined by the same method as described in previous papers[3,5].

* Received June 27, 1990. Correspondence concerning this article should be addressed to S. Goto.

1. Experimentals

The continuous chromatograph apparatus was the same as described in our previous paper[2] except for the addition of the second nozzle to introduce Eluent 2.

The cation exchange resin Dowex 50W-X8 in sodium form was packed to a depth of 470 mm. The resin was sieved in the eluate and a portion of average diameter 0.070 mm was adopted. The void fraction in the bed, ε_B was 0.374. The 0.1 M sodium citrate buffer solutions at pH 3.4 and 4.4 were used as Eluent 1 and Eluent 2 respectively. Feed solutions consisted of glutamic acid, glycine and valine. The feed concentration, C_0, was adjusted to be identical for each amino acid as 20 mol/m^3. The exit concentrations of amino

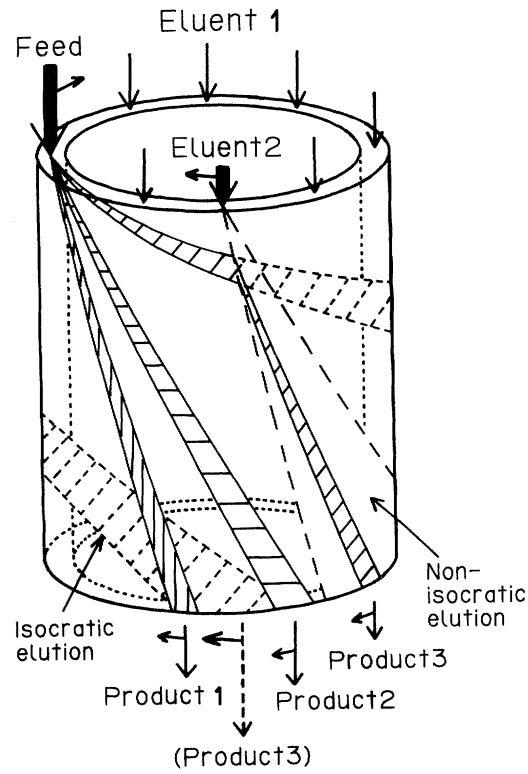

Fig. 1. Principle of continuous rotating annular chromatography with non-isocratic elution

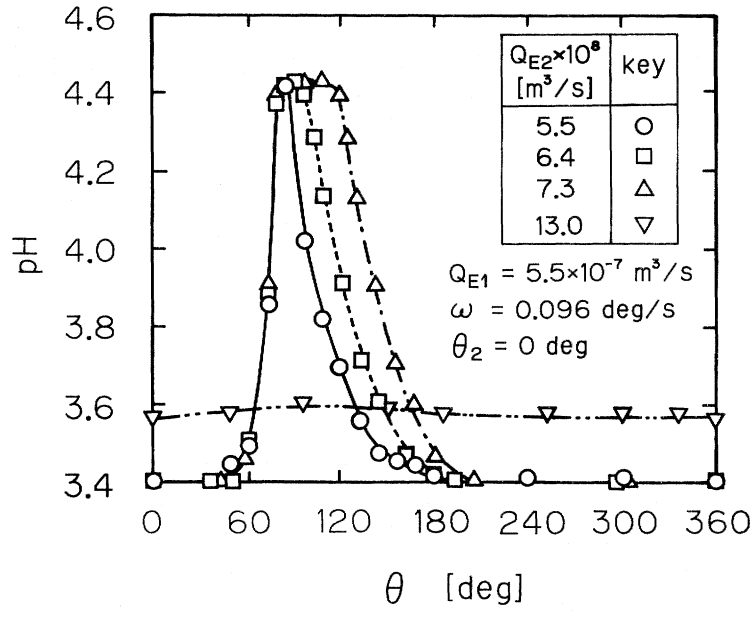

Fig. 2. The pH profile in CRAC

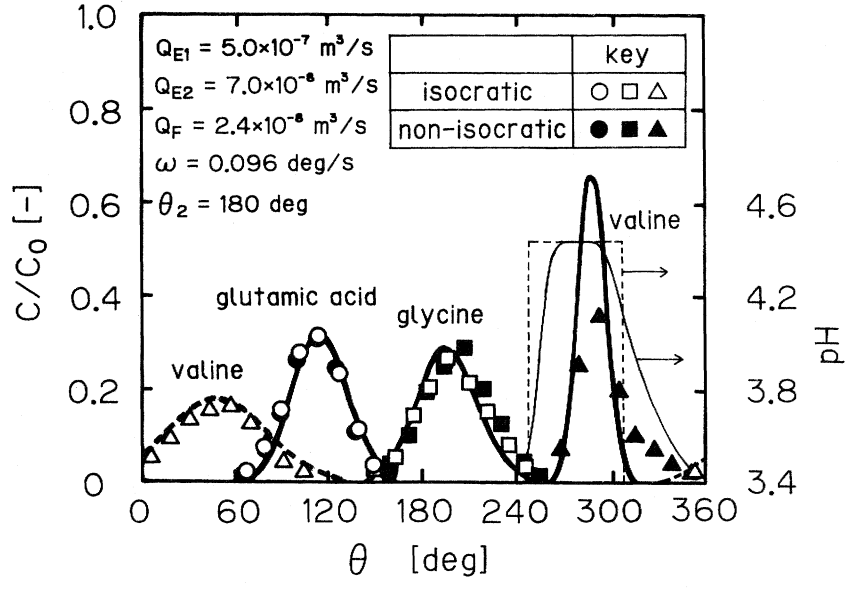

Fig. 3. Comparison between isocratic and non-isocratic elutions

acids were measured by a UV-meter using the ninhydrin method. The exit pH values were measured by a Compact pH Meter (made by Horiba Co. Ltd).

2. Results and Discussion

2.1 The pH profile of CRAC

Figure 2 shows the effect of rate of Eluent 2, Q_{E2} on the pH profiles in CRAC. The rate of Eluent 1, Q_{E1} and the rotating speed, ω, were held constant. Eluent 2 was introduced from only one nozzle with an angular coordinate of zero.

The value of pH was increased from 3.4 to 4.4 at an angular coordinate of about 60 degrees. As Q_{E2} increased, the bandwidth of pH was increased. However, when Q_{E2} increased beyond a certain limit, the solution of Eluent 2 could not flow down the column. In such case, most of the solution flowed upward from the nozzle and mixed with Eluent 1 over the top of the bed. Therefore, the pH profiles became flat at $Q_{E2}=13.0\times10^{-8}\,m^3/s$ in Fig. 2. The limit depended on the ratio Q_{E2}/Q_{E1}, which was about 0.15 in this case.

2.2 Comparison between isocratic and non-isocratic elutions

Figure 3 shows the concentration profiles of amino acids for both isocratic and non-isocratic elutions. The first eluated solute was glutamic acid, the second glycine and the last valine. The peak position of valine

in the isocratic elution appeared after one rotation from the nozzle position and the tail of valine was overlapping the peak of glutamic acid.

On the other hand, valine could be eluated earlier by the introduction of Eluent 2 through the second nozzle at an angular distance of 180 degrees. Then, three components could be separated by the non-isocratic elution. Peak positions of glutamic acid and glycine in this non-isoratic elution are the same as those in the isocratic elution because the pH values in both elutions are kept at 3.4 for angular coordinates from zero to 240 degrees.

The value of pH in the non-isocratic elution was increased from 3.4 to 4.4 for the angular coordinates between 240 and 360 degrees as in the thin solid line of Fig. 3.

The thick lines of Fig. 3 are calculated results by numerical solution. The theory of CRAC with isocratic elution can be described by Eqs. (1)–(8) in the previous paper[2]. Equilibrium constants and kinetic parameters in **Table 1** were used to obtain numerical solutions. The equilibrium constants K could be calculated at pH 3.4 and pH 4.4. Adsorption isotherms measured by the batch wise method were linear. The intraparticle diffusivity $\bar{D}$ and Peclet number Pe were obtained from data at pH 3.4 by the moment method in the previous paper[3,5]. The equilibrium constant K for isocratic elution is kept at the value at pH 3.4 for all angular coordinates. The calculated results shown by thick dotted lines in Fig. 3 are in good agreement with experimental ones for all three amino acids in the isocratic elution (thick dotted lines for glutamic acid and glycine were just overlapped by thick solid lines described later).

For non-isocratic elution, the value of pH may be approximated by the following equations.

$$\text{pH}=4.4 \quad \text{for} \quad \theta_2+\theta_D(z)<\theta<\theta_2+\theta_D(z)+\theta_{E2} \quad (1)$$

$$\text{pH}=3.4 \quad \text{for the other angular coordinates} \quad (2)$$

where the angular delay, $\theta_D(z)$, is a function of the axial coordinate from the top of bed, z, and its given by $\omega z\varepsilon_B/u$. The angular distance of Eluent 2, θ_{E2} is expressed by $2\pi Q_{E2}/(Q_{E1}+Q_{E2}+Q_F)$. Thin broken lines in Fig. 3 indicate these approximate profiles of pH at the bottom of bed while thin solid lines represent the experimental ones. Therefore, the values of K at pH 4.4 in Table 1 were used for angular ranges of Eq. (1). The values of other kinetic parameters were the same as those for the isocratic elution. The peak positions agree well for both experimental and calculated results of all amino acids. However, the calculated profiles of valine are sharper than experimental ones in the non-isocratic elution. As shown by thin solid lines of Fig. 3, there are transition states in experimental profiles of pH. These transitions may affect the concentration profiles of valine in the non-isocratic elution. However, the calculation may be very complex if these transition states of pH are considered.

Table 1. Value of parameters determined at 303 K

		glutamic acid	glycine	valine
K at pH 3.4	[—]	1.18	1.74	2.64
K at pH 4.4	[—]	0.088	0.188	0.211
$\bar{D}\times 10^{11}$	[m²/s]	1.94	4.07	3.58
Pe	[—]	0.078	0.109	0.133

Conclusions

The continuous rotating annular chromatograph (CRAC) with non-isocratic elution could be introduced by adding eluent nozzles as well as the feed nozzle. Three amino acids glutamic acid, glycine and valine—were used as model components. Valine, which was eluated very late and overlapped with glutamic acid for the isocratic elution, could be accelerated by the non-isocratic elution and separated very well. The elution positions could be predicted by a theory. The CRAC with non-isocratic elution was shown to be effective for preparative multicomponent separations.

Nomenclature

C	=	concentration of amino acid in the liquid phase	[mol/m³]
C_0	=	feed concentration	[mol/m³]
$\bar{D}$	=	intraparticle diffusivity	[m²/s]
D_L	=	axial dispersion coefficient	[m²/s]
K	=	adsorption equilibrium constant	[—]
Pe	=	Peclet number ($=2uR_P/\varepsilon_B D_L$)	[—]
Q_{El}	=	first eluent (Eluent 1) rate	[m³/s]
Q_{E2}	=	second eluent (Eluent 2) rate	[m³/s]
Q_F	=	feed rate	[m³/s]
R_P	=	radius of adsorbent particle	[m]
u	=	superficial velocity	[m/s]
z	=	axial coordinate	[m]
ε_B	=	interparticle void fraction in the bed	[—]
θ	=	angular coordinate	[deg]
θ_2	=	nozzle position of Eluent 2	[deg]
ω	=	rotating speed	[deg/s]

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