Breakthrough Curve of Lysine on a Column of a Strong Cation-Exchange Resin of the Ammonium Form

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Abstract

By using a "finite-segment" model for an ion-exchange column, breakthrough curves of ternary cation components—lysine, ammonium, and hydrogen—on a column of a cation-exchange resin of the ammonium form are calculated as a function of limited parameters such as the selectivity coefficients and the dissociation constant of the amino acid. Experimental breakthrough curves on a fixed column packed with Diaion SK-IB (nominal DVB 8%) are simulated and analyzed by the calculated results. Within a limited flow rate of the liquid phase, the model is valid for experimental results, including dependencies on the pH and the ratio of lysine to ammonium, when the conditions of electroneutrality are obeyed.

INTRODUCTION

A fixed-bed apparatus for the ion-exchange adsorption process is commonly used in many industrial plants, such as water treatment, sugar refining, and rare metal recovery (1, 2). Applications have also been made in the treatments of fermentation broths for the recovery and purification of amino acids and antibiotics. Ion-exchange itself is essentially a metathetical chemical reaction of electrolytes between a solution and an ion-exchange resin (3). The ion-exchange process for amino acid purification has many advantage as follows. 1) From the viewpoint of energy saving, this process is regarded to be low in energy requirements compared with the crystallization process. 2) Without any phase change, amino acids are preferably adsorbed onto the resin under appropriate conditions, and at the same time, most of the objectionable impurities are removed. In the fixed-bed column process, it is required to increase the amount of amino acid adsorbed onto the resin as much as possible before the amino acid begins to leak from the resin column, which is called the "breakthrough point" and is determined from the breakthrough curve on the fixed-bed column. In this process the adsorption of amino acid onto the column resin is in an unsteady state and influenced by many factors. Therefore, computed simulations based on a simple general model are unsatisfactory for accurate results. The existence of some cationic species of amino acids affects the shape of the breakthrough curve as well as the amount adsorbed onto the resin.

Breakthrough curves for the adsorption of water and other substances on zeolite and active carbon have been analyzed based on the linear driving force model, which is expressed by a differential equation representing the mass transfer relation under controlled reaction-kinetic rate conditions, taking into account possible variation in equilibrium isotherms for the ion-exchange reaction (4–7). It is required for these treatments to determine some parameters empirically, as well as equilibrium isotherms. An alternative mathematical model for predicting breakthrough curves is the "finite-segment" model, proposed by Levenspiel (8), which can be applied to the adsorption kinetics of a fixed-bed column under periodic countercurrent operations (9). The model has some advantages over the former model. First, some degree of backmixing occurs in most columns of industrial scale, and this model contains an inherent axial dispersion for a more accurate description of the column behavior. Second, the mass transfer equation is much more straightforward.

In this paper the "finite-segment" model is extended to apply to the ion-exchange adsorption process of the ternary component system, including lysine, ammonium ion, and hydrogen ion, and this model thereby demonstrates its utility as an analytical tool for experimental breakthrough

curves. The model is presented in a generalized form to maintain its generality. Although the experimental results available are limited, this analysis provides a convenient tool for investigating the effects of multicomponent cations contained in fermentation broth.

THEORY

A schematic representation of the "finite-segment" model is shown in Fig. 1. The mathematical model derived in this section is based on the following assumptions (*10*): (a) all tanks have the same volume, (b) the liquid phase of each tank is well mixed, and (c) ion-exchange equilibrium for all cations is always established. Although the equations for the model are written for an unlimited number of solutes being adsorbed simultaneously, a ternary system (lysine, ammonium ion, and hydrogen ion) was selected for the present experimental system. In this system the following 12 ionic forms are considered:

In the solution phase L^{2+}, L^+, L^0, L^-, NH_4^+, NH_3, H^+, and OH^-; and in the resin phase $Y\text{-}L^{2+}$, $Y\text{-}L^+$, $Y\text{-}NH_4^+$, and $Y\text{-}H^+$ where L refers to
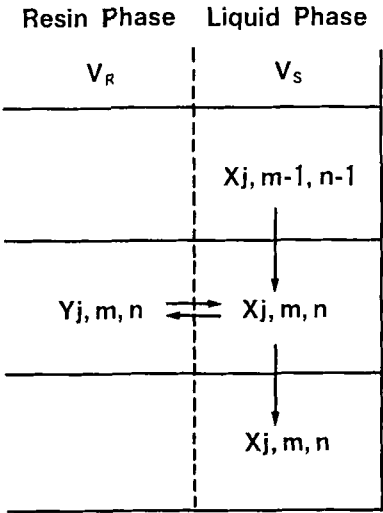

FIG. 1. Schematic representation of segment model:

m number of the feed solution from the top resin
n number of stage (segment)
X_j concentration of J-cation in the liquid phase (mol/L)
Y_j concentration of J-cation on the resin phase (mol/L)
V_R volume of resin in a unit segment (L)

lysine and Y- represents the species in the resin. For the respective components in the system, (a) ion-exchange equilibrium, (b) dissociation equilibrium, (c) material balance, and (d) electroneutrality are derived from the following.

(a) Ion-Exchange Equilibrium

The mass action law is satisfied for any cation J^{l+} with ammonium ion onto the resin and expressed as

$$K_{NH_4^+}^{J} = [Y\text{-}J^{l+}]_{(n,m)}*[X_{NH_4^+}]_{(n,m)}^{l+}/[Y\text{-}_{NH_4^+}]_{(n,m)}^{l+}*[X_J^{l+}]_{(n,m)} \tag{1}$$

where $K_{NH_4^+}^{J}$ indicates the selectivity coefficient for J^{l+}-ion with ammonium ion onto the resin and $[\ ]_{(n,m)}$ refers to the concentration at the n,m-stage phase.

(b) Dissociation Equilibrium in Solution

The dissociation equilibria for respective cationic forms of amino acids (11), ammonium, and water are expressed as follows:

Amino acids:

$$K_1 = [X_{J^+}]_{(n,m)}*[X_{H^+}]_{(n,m)}/[X_{J^{2+}}]_{(n,m)}$$

$$K_2 = [X_{J^0}]_{(n,m)}*[X_{H^+}]_{(n,m)}/[X_{J^+}]_{(n,m)} \tag{2}$$

$$K_3 = [X_{J^-}]_{(n,m)}*[X_{H^+}]_{(n,m)}/[X_{J^0}]_{(n,m)}$$

Ammonium:

$$K_a = [X_{NH_3}]_{(n,m)}*[X_{H^+}]_{(n,m)}/[X_{NH_4^+}]_{(n,m)} \tag{3}$$

Water:

$$K_w = [X_{H^+}]_{(n,m)}*[X_{OH^-}]_{(n,m)} \tag{4}$$

(c) Electroneutrality

In the solution phase:

$$[X_{J^+}]_{(n,m)} + 2[X_{J^{2+}}]_{(n,m)} = [X_{J^-}]_{(n,m)} + 2[X_{J^{2-}}]_{(n,m)} \tag{5}$$

In the resin phase:

$$q = V_r* \left\{ \sum_J [Y_{J^+}] + 2 \sum_J [Y_{J2^+}] \right\} \tag{6}$$

where q is the exchange capacity of the resin employed for a unit segment, and V_r is the volume of the resin in a unit segment.

(d) Material Balance

The material balance is expressed by Eq. (7).

$$V_s*[X_{J^+}]_{(n,m)} + V_r*[Y_{J^+}]_{(n,m)} = V_s*[X_{J^+}]_{(n-1,m-1)} + V_r*[Y_{J^+}]_{(m,m-1)} \tag{7}$$

where V_s is the volume of the solution phase in a unit segment.

CALCULATION WITH A COMPUTER

The method for numerical calculation is described by reference to Fig. 2, which shows a two-dimensional grid system of axes n and m with a mesh of unit dimension; n is a segment number and m is the feed number of the liquid from the top of the resin column. The resin in the $(n, m-1)$ stage is in contact with the liquid phase in the $(n-1, m-1)$ stage and is
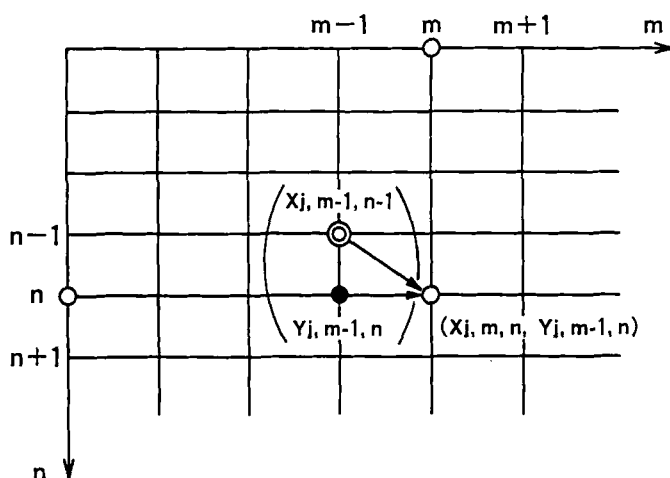

FIG. 2. Finite-difference grids along the bed-length, n, and the cumulative number of feed solutions, m.

allowed to satisfy the ion-exchange equilibrium in the (n,m) stage. At each point of the grid in the (n,m) plane, there are particular values of X_J and Y_J.

It is necessary for a given set of initial conditions to set the boundary values of n and m to enable the calculations to be started. The boundary conditions are given as follows:

At $n = 1$

$$X_{Lys^{l+}(n-1,m-1)} = C_{Lys}, \; X_{NH_4^+(n-1,m-1)} = C_{NH_4^+}^+$$

At $n = m$

$$Y_{J^{l+}(n,m-1)} = 0 \qquad Y_{NH_4^+(n-1,m-1)} = Q$$

where C_{Lys} and $C_{NH_4^+}^+$ are given as the concentrations in the feed solution and Q is the ion-exchange of the resin employed. Abrupt changes in the variable coefficients of the simultaneous equations frequently occurring in every new step cause divergence of the calculation. To avert this, approximate values are set beforehand in this program as follows:

$n = 1$ $Z(J,1,1) = Z(J,1,0)$

$n = m$ $Z(J,n,1) = Z(J,n-1,0)$

Others $Z(J,n,1) = Z(J,n-1,0)$ in the liquid phase

                   $Z(J,n,1) = Z(J,n,0)$ in the resin phase

where $Z(J,n,1)$ is the objective function of J cation in the $n,1$ stage for the calculation relation which is given from Eq. (1) to Eq. (7).

The calculation of Eq. (1) to Eq. (7) was carried out by the Newton-Raphson method. This method is an implicit method of calculation using the partial differential derivative

$$G_{i,j} = dZ_i/dX_{j(n,m)}$$

as a variable coefficient of the simultaneous first-order equation. The first values of the $Z(J,n,m)$ obtained at the previous interval (n,m) are set as an approximate value of $Z(J,n+1,m)$. Subsequent and more accurate values are obtained with a Gauss-Jordan iterative procedure until the successive values of the dependent variables, X_J and Y_J, converge within 10^{-5}.

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                            │    Start    │
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                                   │
                         ┌───────────────────┐
                         │  Allocate Storage │
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                         │   Read data on    │   K, Ki, Vs, V_R, q
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                    │  Allocate initial conditions │
                    │   X(J,1,1),  Y(J,1,1)        │
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                                   │
    ┌──────────────────┐          │                      ┌────────────────────────┐
    │ Iterative for loop│─────────┤                      │  Subroutine            │
    │        M         │          │      ┌───────────┐   │   Newton-Raphson       │
    └──────────────────┘          └──────│ Calculate │◄──│                        │
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        │   For N      │                      │          │   │  Gauss-Jordan   │  │
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                              ◄─────│   Convergence   │
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                                         │ Yes
        ┌──────────────┐      ┌─────────────────────┐
        │  X(J,N,1)    │◄─────│   Print out         │
        │ → X(J,N,0)   │      │ calculated values   │
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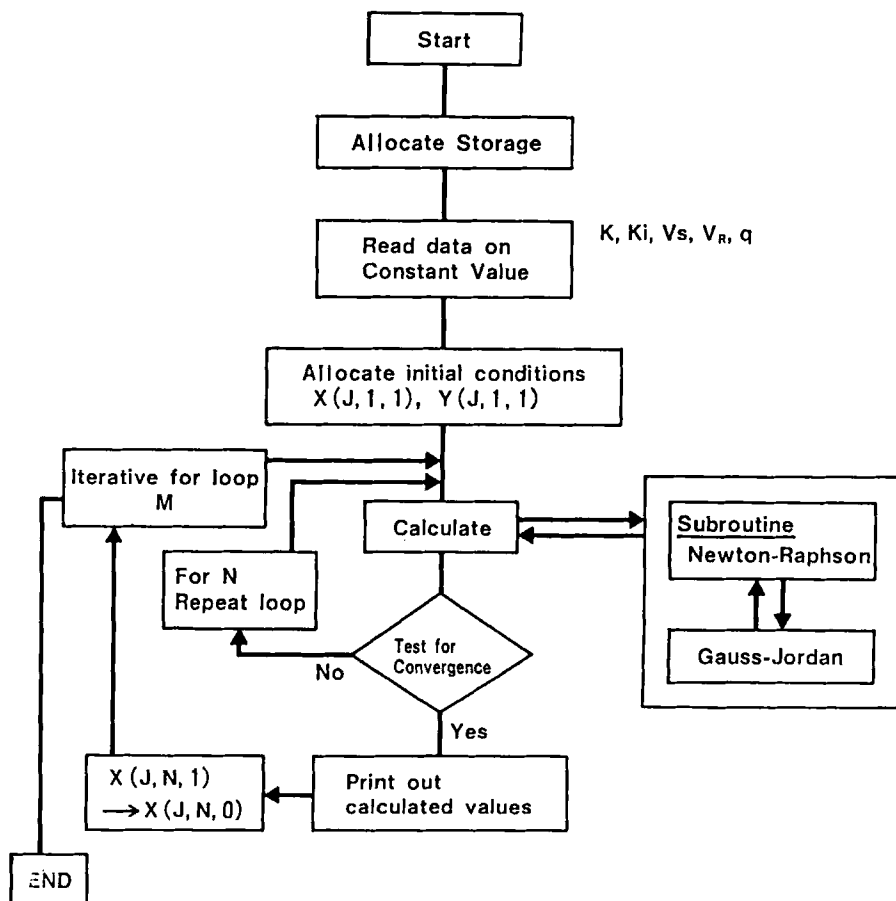
FIG. 3. Computer program sequence of operation.

After calculating the converged values at (n,m), the calculation moves to calculate at $(n+1,m)$ and so on until the end of a specified bed length n and feed volume m. Figure 3 shows the sequence of operations carried out in the calculation. The equations are programmed in BASIC and run on an NEC PC-9801 personal computer.

EXPERIMENTAL

Lysine hydrochloride (pharmaceutical grade) was from Ajinomoto Co., Inc., and ammonium chloride and 35% hydrochloric acid (reagent grade) were purchased from Wako Junyaku Co. These reagents were used without further purification.

The resin employed was Diaion SK-IB (nominal DVB content 8%) purchased from Mitsubishi Kasei Kogyo Co. The resin was packed in the column and converted to the ammonium form by passing dilute ammonia in water through the column. The ion-exchange capacity of the resin was determined from a measurement of the amount of ammonium ion removed by exhaustive displacement with dilute sodium chloride. The void volume, e, was obtained from

$$e = V_w/\overline{V}_0$$

where $\overline{V}_0$ is the bed volume of resin and V_w is the volume of water contained in the bed. These values were measured as follows: 30 mL ($\overline{V}_0$) of the cation-exchange resin of the ammonium form was poured into the column (10 mm in diameter) and the level of water was brought to the top of the resin bed. The water was drained from the column by pressure with air, and the volume of the water (V_w) was measured.

Validation of the Proposed Model

A schematic experimental flow diagram is shown in Fig. 4. Ammonium form resin (40 mL) was poured into each of 10 glass columns (20 mm in
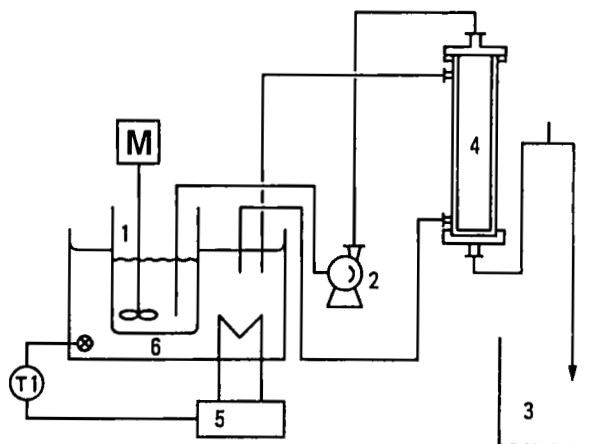

FIG. 4. Experimental apparatus.

1: 5-L glass beaker for prepared solution
2: proportional pump for feeding of solution
3: 10-L plastic-basket for purged liquid
4: polystyrene resin column with jacket
5: heater with thermostat
6: water bath with thermometer

diameter, 160 mm in height) connected in series, which is equivalent to each stage of the 400 mL resin in a column divided by 10. The solution, stored in a storage tank (1 in Fig. 4), was fed to the column for several runs via a peristaltic pump (2 in Fig. 4) with which the feed rate was controlled.

(1) Effect of the Ratio of Lysine to Ammonium Ion in the Feed Solution at pH 2.0 on the Amount of Adsorbed Lysine

Lysine hydrochloride (22 g) and ammonium chloride (0, 6.4, or 12.8 g) were added to 300 mL distilled water, and each sample was adjusted to pH 2.0 with 35% hydrochloric acid and made up to 400 mL with distilled water. The concentration of chloride ion, which was employed as the anion in Eq. (5) for simulation, was measured by the Forhart titration method. These solutions were stored in tank 1 in Fig. 4 and were passed through the column at a flow rate of 40 mL/h, which is equivalent to a space velocity of 1.0. The 10 columns were separated, and then 100 mL distilled water was passed through each column to remove any excess solution remaining in the column. Then the effluent was collected and measured for lysine, ammonium ion, and pH, following which each resin column was eluted with 80 mL of 2 N hydrochloric acid solution and each eluate obtained was measured for the same items as was the effluent, except for pH.

(2) Effect of the Feed Rate on the Amount of Adsorbed Lysine

The composition of the feed solution was fixed as follows: lysine hydrochloride was 0.3 mol/L, ammonium chloride was 0.3 mol/L, and the pH was 2.0, adjusted with 35% hydrochloric acid, and the total volume was made up to 400 mL with distilled water. The flow rate was varied with a peristaltic pump. After the solution was passed through, each of the 10 resin columns was separated and followed by the same operations mentioned above.

(3) Breakthrough Curve for Ternary Cations in the Solution

Instead of 10 columns in series (3 in Fig. 4), a glass column (20 mm in diameter and 400 mm in height) was used. Three feed solutions containing lysine hydrochloride (0.3 mol/L) and ammonium chloride (0.3 mol/L) were prepared by adjusting the pH to 1.0, 2.0, and 6.0, respectively, with 35% hydrochloric acid.

Precisely 100 mL of the ammonium form resin was poured into the glass column. 1.0 L of each prepared solution was passed through the column at a flow rate of 100 mL/h while maintaining the level of water at the top of the resin bed. Effluent was taken from the bottom of the column at 30-min intervals and the pH was measured immediately afterwards with a pH

meter (Toa Electronics Ltd. Model HM-30) and stored at 263 K, after adding a few drops of 35% hydrochloric acid, until the ammonium and lysine analyses were made. The column temperature was maintained at 298 K during the experiment by circulating water through a jacket.

RESULTS AND DISCUSSION

The properties of the cation-exchange resin used were as follows: the ion-exchange capacity of the ammonium form resin was 1.93 mol/L and the void volume, e, was 0.40.

(1) Effect of the Ratio of Lysine to Ammonium Ion in the Feed Solution at pH 2.0 on the Amount of Adsorbed Lysine

In the present analysis of ion-exchange data, the selectivity coefficients of lysine ions and hydrogen ions on the 8% DVB ammonium form cation-exchange resin are assumed to be independent of changes in the concentrations of other solutions at 298 K, and these values are given as follows (12):

$$K_{NH_4^+}^{Lys^+} = 0.40, \qquad K_{NH_4^+}^{Lys^{2+}} = 5.87, \qquad K_{NH_4^+}^{H^+} = 0.46$$

The experimental results on the amount of adsorbed lysine obtained from the runs carried out with 10 columns in series are shown in Fig. 5, with a comparison of calculated results in which $[Y_{-Lys}]_{calcd.}$ is obtained from

$$[Y_{-Lys}]_{calcd.} = K_{NH_4^+}^{Lys^+}[X_{Lys^+}]\{[Y_{-NH_4^+}]/[X_{NH_4^+}]\}$$

$$+ K_{NH_4^+}^{Lys^{2+}}[X_{Lys^{2+}}]\{[Y_{-NH_4^+}]/[X_{NH_4^+}]\}^2 \quad (8)$$

where $[X_{Lys^+}]$, $[X_{Lys^{2+}}]$, $[X_{NH_4^+}]$, and $[Y_{-NH_4^+}]$, are from the experimental data. It is seen from Fig. 5 that the calculated values of $[Y_{-Lys}]$ correlate fairly well with the observed ones. It was found from this result that the values of the selectivity coefficient remained constant within the range of solute concentrations used in this experiment. Figure 6 shows the experimental results of both the amount of adsorbed lysine onto the resin and the concentration of lysine in the effluent plotted against the number of resin columns with various values for the ratio $[X_{Lys}]/[X_{NH_4^+}]$ in the feed solution. The theoretical curves obtained from the computer simulation reproduced the experimental curves rather well. As the ratio $[X_{Lys}]/[X_{NH_4^+}]$ increases, the value of the amount of adsorbed lysine on the first resin column increases as expected from Eq. (8), and the values coincide with those obtained from Eq. (8). This result means that the contact of the resin with
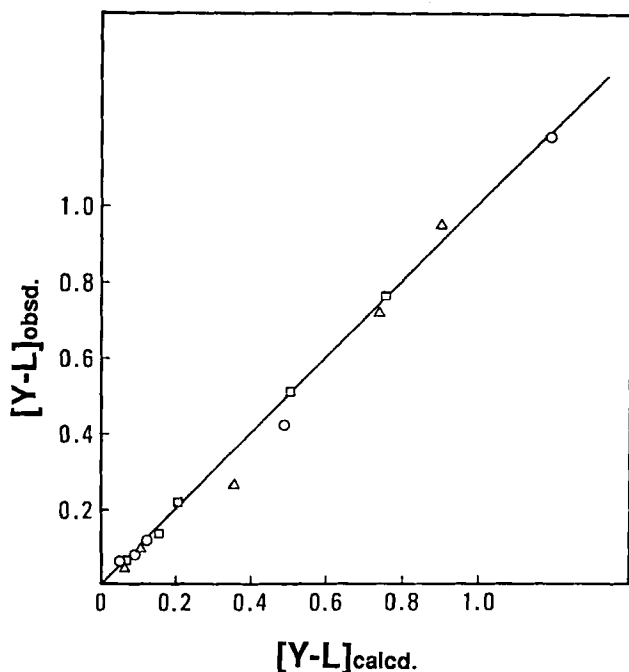
FIG. 5. Comparison of calculated and experimental results of [Y-L] at pH 2.0.

a 10-bed volume of feed solution reaches a state of equilibrium in both phases. Incidentally, the degree to which the resin column was divided, n = 10, was sufficient to simulate adsorption behavior in the resin column.

(2) *Effect of the Feed Rate on the Amount of Adsorbed Lysine*

In the present model, the effect of the flow rate was not explicitly expressed because ion-exchange equilibria are always assumed to be established for each resin column. Therefore, it is necessary to evaluate the limitations of this model for actual applications. Figure 7 shows a comparison of the observed amounts of both lysine and ammonium adsorbed in each column within a flow rate range of 0.5 to 4.0 h^{-1} by using the space velocity (SV) and the calculated values as a function of the column number, neglecting the effect of flow rate. With an increase in the flow rate greater than 1.0 h^{-1} as SV, the experimental values gradually deviated from the calculated value of 0.88 mol/L; that is, the experimental results of the amount of adsorbed lysine on the first column are summarized as follows; that for SV = 0.5 was 0.89 mol/L, that for SV = 1.0 was 0.91 mol/L,
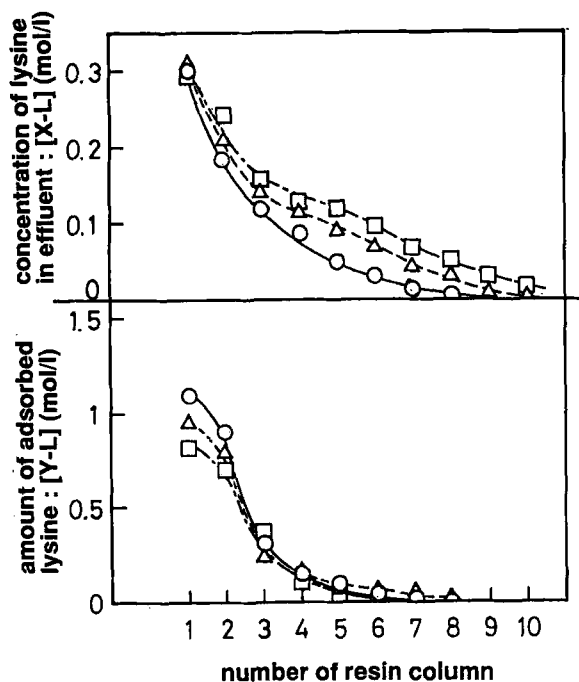
FIG. 6. Comparison of the experimental and calculated values of both [Y-L] on the resin and [X-L] in the effluent for each column as a function of $[Lys/NH_4^+]$ in the feed solution:

Units (mol/L)

Lys	NH_4^+	pH	Experimental	Calculated
0.3	0	2	○	——
0.3	0.3	2	△	- - -
0.3	0.6	2	□	- - -

that for SV = 2.0 was 0.84 mol/L, and that for SV = 4.0 was 0.81 mol/ L. From the results in Fig. 7, we found that the ion-exchange zone (the mass transfer zone in the column) increased in length with an increase in the flow rate due to the lowering of metathetical chemical interactions caused by an increase in the flow rate. It follows that, strictly speaking, the application of this model is limited at flow rates lower than 1.0 h^{-1} as SV. However, the extent of deviation of the amount of adsorbed lysine from the calculated value was within 5% at a flow rate of 2.0 as SV. From this result it seems permissible for industrial applications to simulate the breakthrough curves at lower flow rates based on the present model.
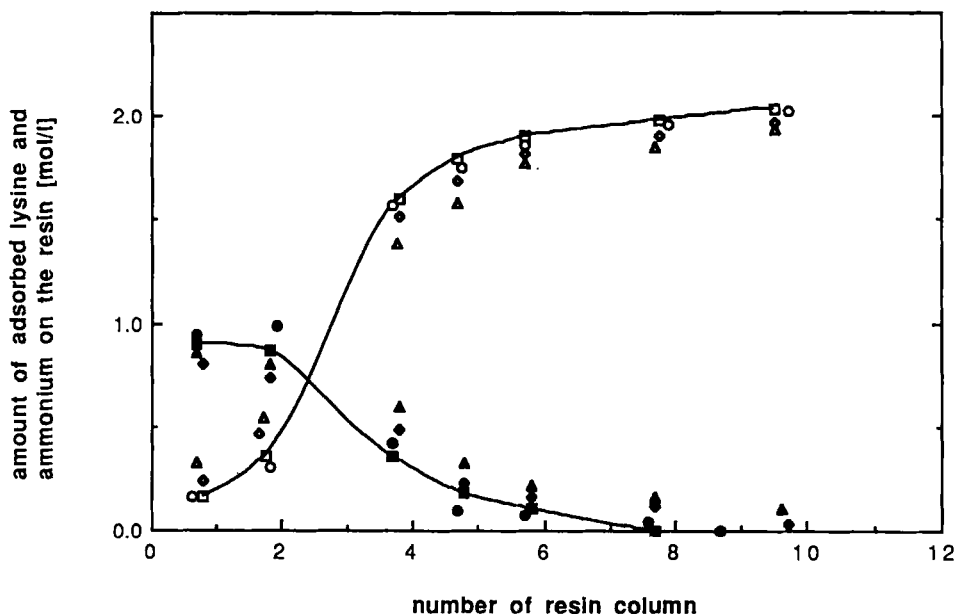
FIG. 7. Effect of the feed rate on the amount of adsorbed lysine and ammonium on the resin
as a function of the relative volume of effluent:

SV	Lysine	Ammonium ion
0.5	○	●
1.0	□	■
2.0	◇	◆
4.0	△	▲

(3) Breakthrough Curve

Figures 8 to 10 show breakthrough curves plotted against the relative
bed volume of effluent with various values of the feed solution pH at a
flow rate of $1.0 \ h^{-1}$ as SV. The calculated curves for each pH value are in
fairly good agreement with the experimental curves. Since the sample point
for the experimental column was in the vicinity of the outlet tube, a small
amount of mixing would cause an unsharpening effect on the breakthrough
point. Certain irregularities among pH and ammonium ion were recog-
nized at the beginning of the relative bed volume. This could be caused
by incomplete mixing in the downstream side of the column and by an
abrupt change in the resin volume due to the effect of lysine adsorption
on changes in the osmotic pressure, which is estimated to be a decrease
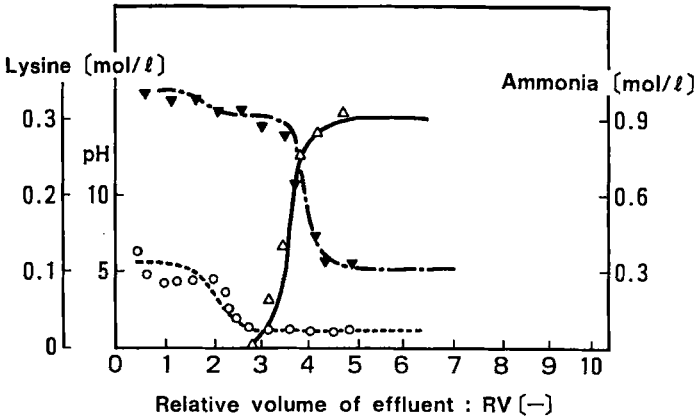of 10% from the ammonium form to the lysine form; an equivalent of 0.91

FIG. 8. Simulation of breakthrough curve for each component compared with that obtained from experiment at pH 1.0. Lysine (△), ammonium ion (▼), pH (○).

mol/L of the amount of adsorbed lysine from the ammonium form resin. Electroneutrality as well as the selectivity coefficient for mono- and divalent forms of lysine and hydrogen are important factors for the prediction of the breakthrough curve, since these influence pH values through changes in the equilibrium conditions.
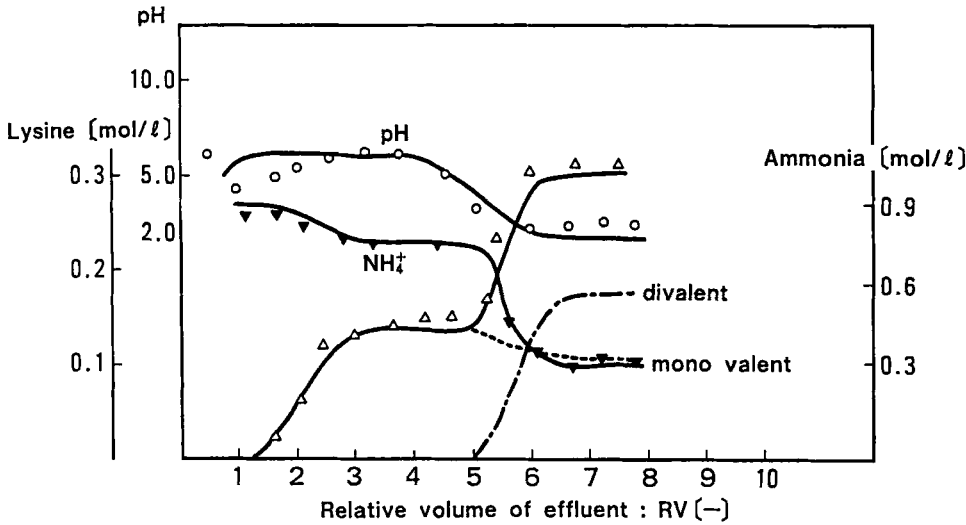
FIG. 9. Simulation of breakthrough curve for each component compared with that obtained from experiment at pH 2.0. Lysine (△), ammonium ion (▼), pH (○), monovalent lysine (- - -), divalent lysine (— · —).
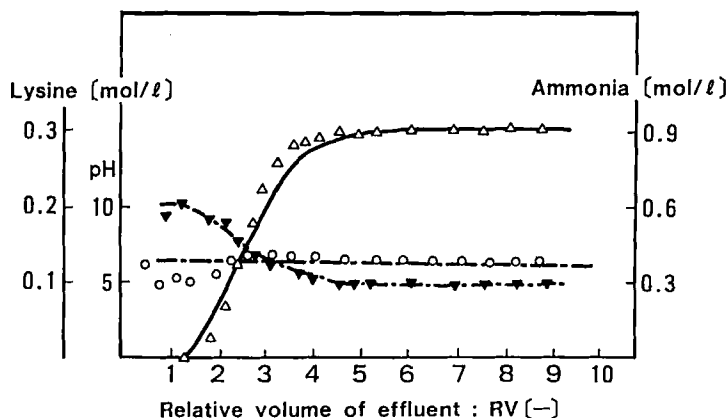
FIG. 10. Simulation of breakthrough curve for each component compared with that obtained from experiment at pH 6.0. Lysine (△), ammonium ion (▼), pH (○).

It is of interest that the calculated breakthrough curve of lysine at pH 2.0 shows the possibility of chromatographic separation of mono- and divalent lysine cations. This mechanism is assumed to be as follows: The ratio of mono- and divalent lysine cations in the feed solution is 0.387 to 0.613; at the first stage of lysine adsorption in the column, divalent lysine adsorbed preferentially to the resin and liberated two equivalents of ammonium ion, which is designated in the following stoichiometric relation:

$$[X_{Lys^{l+}}] + l*[Y_{-NH_4^+}] = [Y_{-Lys^{l+}}] + l*[X_{NH_4^+}] \qquad (9)$$

where l is the valence of lysine cations. This liberated ammonium ion hydrolyzes water, based on a strong acid/weak base reaction, and liberates hydrogen ions at the concentration shown in (9).

$$[H^+] = K_w[X_{NH_4^+}]/K_a \qquad (10)$$

From Eq. (10), the pH calculated in the effluent was 4.7, which coincides with the experimental value. At this pH, only monovalent lysine was detected in the effluent. As the feed volume of solution increased, the pH in the effluent began to decrease owing to the decrease in the liberation of ammonium ion, which affected the pH of the effluent. Finally, both mono- and divalent lysine were detected in the effluent with decreasing pH of the effluent.

It is interesting to compare the breakthrough curve of lysine at pH 1.0 with that at pH 6.0. At pH 1.0, more than 95% of the lysine in the feed

solution was divalent, and at pH 6.0, 100% of the lysine was monovalent. The breakthrough curve at pH 1.0 was steeper than that at pH 6.0 owing to the higher selectivity coefficient of divalent lysine compared with the monovalent form.

It follows from the present investigation that breakthrough curves under various conditions, such as changes in pH and the ratio of concentrations of lysine and ammonium ions, can be predicted from stoichiometric calculations on the basis of a limited numbers of parameters, such as the selectivity coefficient with electroneutrality.

Acknowledgment

NOMENCLATURE

C	concentration of cation in feed solution (mol/L)
e	void volume of resin (—)
$G_{i,j}$	partial differential derivative of Newton-Raphson method used in simulation
$K_{NH_4^+}^J$	selectivity coefficient for J-cation on the ammonium form of resin
K_i	dissociation constant of i-ion
Q	ion-exchange capacity of resin (mol/L)
q	ion-exchange capacity of resin contained in unit segment (mol)
SV	space velocity (h^{-1})
V_0	volume of resin in a column obtained from void volume measurement (L)
V_R	volume of resin in unit segment (L)
V_S	volume of liquid phase in unit tank (L)
V_w	exhaustive volume of water obtained from void volume measurement (L)
[X-J]	concentration of J-cation in the solution phase (mol/L)
[Y-J]	concentration of J-cation on the resin phase (mol/L)
Z	objective function of Eqs. (1) to (8)

Subscripts and Superscripts

a	ammonium ion
l	valence of amino acid ion; + cation, − anion
n	number of divided units in the resin column; the number of segments
m	the imaginary feed number for the feed solution on the resin
w	water

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