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Elution Kinetics of Lysine from a Strong Cation-Exchange Resin with Ammonia Water

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Abstract

The elution mechanism of lysine with ammonia water was investigated. In alkaline pH regions of the liquid phase, the effect of Donnan membrane equilibrium on the elution of lysine adsorbed onto the resin was found to be a predominant factor in determining the equilibrium kinetics in terms of the mass action law for adsorption.

INTRODUCTION

Analysis of the elution process of lysine by using a strong cation-exchange resin is important for the optimum recovery of lysine from lysine fermentation broth on an industrial scale. Lysine adsorbed onto the resin is eluted with ammonium water and simultaneously the ionic form of resin is converted from the lysine form to the ammonium form. In a previous paper (*1*) we discussed the ion-exchange equilibrium on the basis of the mass action law in order to predict the equilibrium amount of lysine adsorbed onto the resin by taking account of the component of the lysine fermentation broth.

For this purpose we also investigated the selectivity coefficients of such cations as amino acids, inorganic ions, and colored substances contained in the lysine fermentation broth against the ammonium ions on the resin (*2*, *3*). As the amino acid is amphoteric, the ratio of its cationic form changes with a change in the pH of the solution. The optimum pH of the broth for the adsorption of lysine onto the resin depends on the composition of cations in the broth. For example, when molasses is used as a raw material for lysine fermentation, an acidic pH region where lysine exists as the divalent ionic form is selected to obtain the maximum amount of lysine adsorbed onto the ammonium form resin, because the selectivity coefficient of divalent lysine is much larger than that of other cations. In fact, other monovalent cations are inhibited from adsorption by the divalent lysine cations at equilibrium in acidic solution. An investigation of the elution kinetics of lysine adsorbed onto the resin with ammonium water is necessary to determine the optimum elution conditions.

In this paper we examine the elution process of lysine on a resin with ammonia water and discuss the elution mechanism based on ion-exchange equilibrium and taking into account the Donnan membrane equilibrium.

EXPERIMENTAL

Materials

The strong cation-exchange resin, Diaion SK-IB, was purchased from Mitubishi Kasei Kogyo Co. and converted to the ammonium form by treating it with an excess volume of ammonia water. Ammonia water (28%) and a 35% hydrochloric acid reagent grade solution were purchased from Wako Junyaku Kogyo Co.

Procedures

Loading of Cations on the Cation-Exchange Resin in Equilibrium with Lysine Fermentation Broth by a Column Method

An acrylic column of 50 cm length and 5 cm diameter was used as the resin column. A perforated plate made of acrylic resin with 30 mesh Teflon cloth was used as the resin stopper. The flow rate of the feed broth was measured by a rotor meter calibrated by water flow. Cation-exchange resin (500 mL) in the ammonium form was fed from the top of the column and mixed with deionized water from the bottom of the column to avoid air bubbling. The broth to be fed to the resin column was adjusted to pH 1.8 or 4.0 with 35% hydrochloric acid and stocked in a feed tank. Ten bed volumes of broth were fed to the resin column at a rate of SV 2.0, and then 5 bed volumes of deionized water were passed through the resin.

The amount of cation adsorbed onto the resin was determined from analysis of the cation concentration in the eluate with a 2-*N* hydrochloric acid solution.

Batch Elution Equilibrium Studies

The elution experiments were carried out by a batch method. Accurately measured volumes (in the range of 20 to 50 mL) of the resins saturated with the lysine fermentation broth were placed in Erlenmeyer flasks of 300–1000 mL capacity and immersed in 2 *N* ammonia water. The volume ratio of ammonia water to resin was changed from 0.5 to 30. The flask with a rubber stopper was set in a water bath with a thermostat (Yamato Kagaku Co., Model 410) and was kept at 298 K with shaking for about 24 h. After equilibration, aliquots of the supernatant were separated from the resin by filtration under reduced pressure for the determination of lysine, pH, and inorganic ions. The separated resin was packed in a column (1.25 cm diameter) and then eluted with 10 bed volumes of 2 *N* hydrochloric acid at a flow rate of SV 2.0. The column effluent and subsequent eluates with 3 bed volumes of deionized water were collected in a 1000-mL flask for analysis of the respective cation concentrations.

Analysis

Lysine was analyzed by using an amino acid analyzer (Model Hitachi 450). Ammonium nitrogen was measured by the alkaline distillation method, total nitrogen was measured by the Kjeldahl method, and inorganic ions were analyzed by atomic flame adsorption spectrometry (Nihon Jailly Kogyo Co.).

RESULTS AND DISCUSSION

Cation Compositions Adsorbed on the Resin

Table 1 gives the amount of each cationic species adsorbed onto the ammonium form resin at equilibrium with the lysine fermentation broth at pH 1.8 or 4.0. The amount of adsorbed lysine on the resin at pH 1.8 was 1.87 times larger than that at pH 4.0. At pH 1.8, the ionic form of lysine was mostly divalent, and the divalent lysine cation repressed the adsorption of inorganic ions, such as potassium and sodium ions. On the other hand, at pH 4.0, larger amounts of inorganic ions were adsorbed

TABLE 1

Equilibrium Amounts of Cations Adsorbed on the Strong Cation-Exchange Resin at pH 1.8 and 4.0 (units: mol/L)

	1.8	4.0
Lysine	0.602	0.323
Total nitrogen	1.673	1.485
Ammonia nitrogen	0.356	0.769
Potassium	0.32	0.575
Sodium	0.06	0.141
Calcium	0.0075	0.021
Ion-exchange capacity	1.94	1.94

onto the resin, since divalent lysine cations were less than 0.5% of the total lysine. It is apparent from a comparison of the values of the residual amount of ammonium ion at equilibrium with the lysine broth that the resin exchange sites were more than twice as occupied at pH 1.8 as at pH 4.0. This was mainly due to the weak affinity of monovalent lysine cations to the resin.

Effect of the Ammonia Solution pH at Equilibrium on the Residual Amount of Lysine on the Resin

The Selectivity Coefficient of Lysine for Ammonium Ion in Alkaline Solution

In a previous paper we reported the selectivity coefficients of several kinds of cationic species containing amino acids, where a colored substance derived from molasses was used as a raw material for the lysine fermentation broth, and we discussed the mechanism of the adsorption process based on ion-exchange equilibrium and the mass action law. Based on that investigation, it is evident that the saturated amounts of respective cations on the strong cation-exchange resin can be calculated from simultaneous electroneutrality equations on the resin phase in terms of the mass action law with previously determined selectivity coefficients.

First, in order to study the similarity of the elution mechanism with that of adsorption, the residual amount of lysine at equilibrium in the elution process with ammonia water is examined based on the mass action law. The selectivity coefficients of the respective cationic species for ammonium ion are defined and the equilibrium equation (1) is derived from the electroneutrality on the resin as follows:

$$[\text{R-lys}]_{\text{clcd}} = [\text{R-NH}_4^+]_{\text{obsd}}\{1 + K^{\text{A}^+}_{\text{NH}_4^+}(\text{A}^+)_S/(\text{NH}_4^+)_S\} \qquad (1)$$

where $[\text{R-NH}_4^+]_{\text{obsd}}$ is the experimental value of the residual amount of ammonium ion on the resin, and $(\text{A}^+)_S$ and $(\text{NH}_4^+)_S$ are the respective values of A^+-cations and ammonium ion in solution at equilibrium. $K^{\text{A}^+}_{\text{NH}_4^+}$ is the selectivity coefficient of A^+ cation for the ammonium form, 0.4 for monovalent lysine ion, 1.15 for potassium ion, and 0.87 for sodium ion.

Figure 1 shows a comparison of the logarithmic values of [R-lys] measured experimentally and that calculated from Eq. (1) as a function of the equilibrium solution pH, when lysine broth with pH 1.8 or 4.0 was fed to the resin during the adsorption process. In spite of the difference in the saturated amount of cation on the resin, the relationship between the logarithmic value of [R-lys] and the final pH at equilibrium was in good agreement with the various resins prepared at different pHs in the ad-

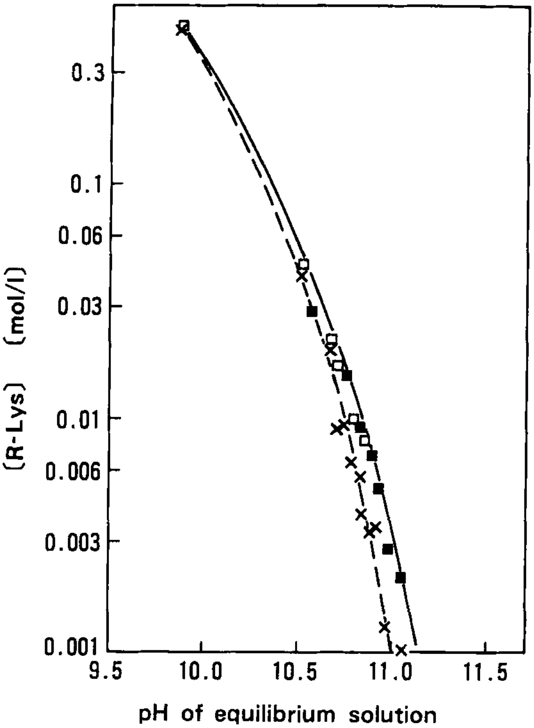

FIG. 1. Comparison of the calculated and the observed values of residual lysine on the resin as a function of the equilibrium pH of the solution. Experimental values: (□) adsorption pH at 1.8, (■) adsorption pH at 4.0. (×) Calculated value based on the mass action law using both $K_{NH_4^+}^{lys^+} = 0.4$ and the concentration of monovalent lysine determined from the solution pH.

sorption process. However, the logarithmic value of [R-lys] obtained experimentally coincided with that calculated at pH 9.8 and gradually began to deviate from the value calculated by using Eq. (1) with an increase in solution pH.

In order to verify the selectivity coefficient values for the respective cations, we calculated these selectivity coefficients by substituting the experimental values of the respective equilibrium cation concentrations into Eq. (2):

$$K_{NH_4^+}^{A^+} = [R\text{-}A^+]C_{NH_4^+}/[R\text{-}NH_4^+]C_{A^+} \qquad (2)$$

Figure 2 shows the relationships between the calculated selectivity coefficients of the respective cations for the ammonium ion and the pH of the

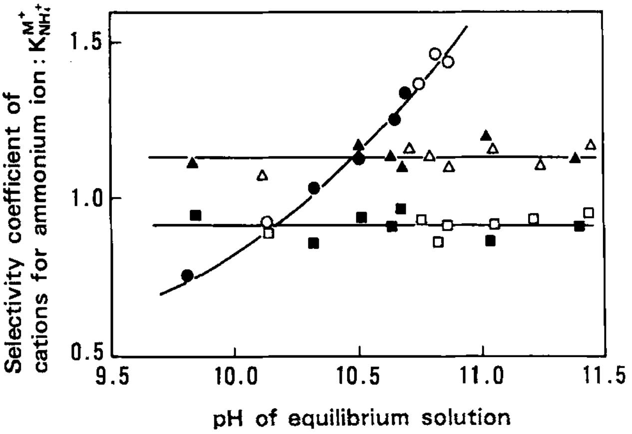

FIG. 2. Selectivity coefficients for cations determined from experiments:

Adsorption pH		
1.8	4.0	
○	●	Monovalent lysine
□	■	Sodium
△	▲	Potassium

equilibrium solution. The values for the selectivity coefficients of inorganic cations remained constant within the acceptable range of experimental error in the pH range tested; 1.13 for potassium ion and 0.91 for sodium ion. These values were in good agreement with those used in this procedure. However, the selectivity coefficient of monovalent lysine varied from 0.7 to 1.5 with an increase in the solution pH and deviated from the value of 0.4. The relationship between the selectivity coefficient of monovalent lysine ($K^{\mathrm{lys}^+}_{\mathrm{NH}_4^+}$) and the concentration of hydrogen ion, $(\mathrm{H}^+)_S$, is expressed by the following empirical relation in the alkaline pH range:

$$\log K^{\mathrm{lys}^+}_{\mathrm{NH}_4^+} = -2.68 - 0.265 \log (\mathrm{H}^+)_S \tag{3}$$

From these results it was shown that the selectivity coefficient of monovalent lysine increases exponentially with an increase in the pH of the solution. It is clear that factors other than the mass action relationship exert an influence on the elution mechanism of lysine from the resin in an alkaline pH range.

Application of the Donnan Membrane Equilibrium

The Donnan membrane equilibrium principle was applied to ion-exchange phenomena on ion-exchange resins. Anions such as OH^- ions are effectively excluded from the insides of strong cation-exchange resins owing to the Donnan ion exclusion mechanism (*4*). This effect is expected to cause some difference in the pH between the resin phase and the solution phase; the pH of the resin phase is presumed to be more acidic than that of the solution.

In order to make a quantitative analysis of the elution phenomena, the Donnan ion exclusion mechanism should be taken into consideration. The situation is represented by the model shown in Fig. 3. The following two assumptions, which are intuitive rather than experimentally determinable, were made: 1) the lysine anion and hydroxy anion are controlled by Donnan membrane equilibrium between the resin phase and solution phase, and 2) the amounts of the respective ionic species adsorbed onto the resin at equilibrium are determined by the mass action law for ion-exchange equilibrium with the selectivity coefficient of each cation species.

It is now possible to derive the kinetic relationship of an elution process employing a batch method by considering Donnan membrane equilibrium as follows.

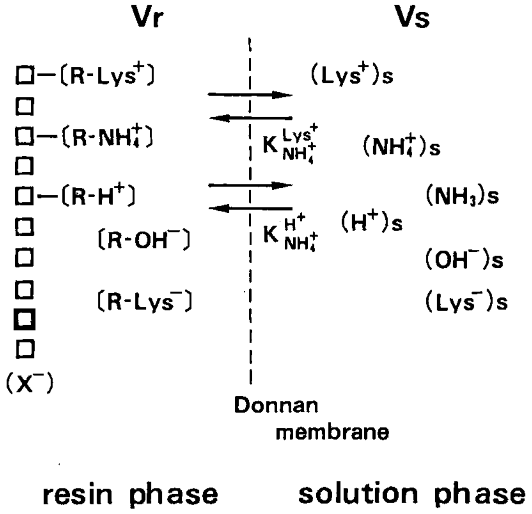

FIG. 3. A model of the elution process of lysine with ammonia water in alkaline pH regions.

Donnan Membrane Equilibrium and Electroneutrality in Both Phases

$$Y_R^+ = [\text{R-lys}^+] + [\text{R-NH}_4^+] + [\text{R-H}^+]$$

Equality of chemical potential:

$$(Y_R^+)([\text{R-lys}^-] + [\text{R-OH}^-])$$
$$= ((\text{lys}^+)_S + (\text{H}^+)_S + (\text{NH}_4^+)_S)((\text{OH}^-)_S + (\text{lys}^-)_S) \quad (4)$$

Electroneutrality: Resin phase:

$$Y_R^+ = (\text{X}^-) + [\text{R-OH}^-] + [\text{R-lys}^-] \quad (5)$$

and Solution phase:

$$(\text{lys}^+)_S + (\text{NH}_4^+)_S + (\text{H}^+)_S = (\text{OH}^-)_S + (\text{lys}^-)_S \quad (6)$$

where (X^-) shows the ion-exchange capacity of ammonium form resin.

Ion-Exchange Equilibrium in the Resin Phase

$$K_{\text{NH}_4^+}^{\text{lys}^+} = [\text{R-lys}^+](\text{NH}_4^+)_s/[\text{R-NH}_4^+](\text{lys}^+)_s \quad (7)$$

$$K_{\text{NH}_4^+}^{\text{H}^+} = [\text{R-H}^+](\text{NH}_4^+)_s/[\text{R-NH}_4^+](\text{H}^+)_s \quad (8)$$

Dissociation Equilibria of Lysine, Ammonia, and Water

$$k_1 = (\text{lys}^0)_S(\text{H}^+)_S/(\text{lys}^+)_S \quad (9)$$

$$k_2 = (\text{lys}^-)_S(\text{H}^+)_S/(\text{lys}^0)_S \quad (10)$$

$$k_a = (\text{NH}_3)_S(\text{H}^+)_S/(\text{NH}_4^+)_S \quad (11)$$

$$k_w = (\text{H}^+)_S/(\text{OH}^-)_S \quad (12)$$

Material Balance of the Respective Species

$$V_R[\text{R-lys}]_0 = V_R\{[\text{R-lys}^+] + [\text{R-lys}^-]\}$$
$$+ V_S\{(\text{lys}^-)_S + (\text{lys}^0)_S + (\text{lys}^+)_S\} \quad (13)$$

$$V_R[\text{R-NH}_4^+]_0 + V_S(\text{A-N})_0$$
$$= V_R[\text{R-NH}_4^+] + V_S\{(\text{NH}_4^+)_S + (\text{NH}_3)_S\} \quad (14)$$

$$V_R[\text{R-H}^+)_0 + V_S(\text{H}^+)_0 = V_R[\text{R-H}^+] + V_S(\text{H}^+)_S \quad (15)$$

These equations were simultaneously solved by using the Gauss–Jordan technique on an NEC 9801E personal computer. By substituting the initial values for V_R, V_S, $[\text{R-lys}]_0$, $[\text{R-NH}_4^+]_0$, $[\text{R-H}^+]_0$, and $(\text{A-N})_0$, we obtained the equilibrium values under various experimental conditions.

Figure 4 shows the relationship between the pH of the resin phase obtained by simulation and the pH in solution. It is seen from Fig. 4 that the resin phase was more acidic than the solution, as expected, and the difference in pH gradually became larger with an increase in the pH of the solution. With a solution pH greater than 10.8, the pH in the resin phase asymptotically approached a constant value of 9.9. From Eq. (8), the pH of the resin phase is

$$\begin{aligned} p[\text{R-H}^+] &= -\log\,[\text{R-H}^+] \\ &= -\log K_{\text{NH}_4^+}^{\text{H}^+} + \log\,(\text{NH}_4^+)_s - p(\text{H}^+)_s \qquad (16) \end{aligned}$$

By substitution of the experimental values and the selectivity coefficient of hydrogen ion into Eq. (16), we obtained the same $p[\text{R-H}^+]$ value of

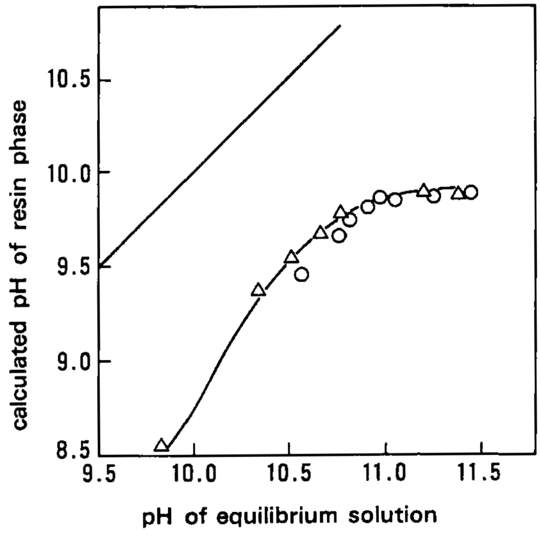

FIG. 4. The calculated pH of resin phase and the selectivity coefficient of monovalent lysine against ammonium ion:

Adsorption pH	Symbol
1.8	△
4.0	○

9.7–9.9 at a solution pH greater than 10.8. It is evident from this result that the degree of acidity in the resin phase is a function of the concentrations of ammonium ion and hydrogen ion which are affected by Donnan membrane equilibrium at equilibrium. The ratio of monovalent anion lysine to monovalent cation lysine in the resin phase, [R-lys$^-$]/[R-lys$^+$], which was obtained from the simulation, against the pH of the solution is shown in Fig. 5. The value of [R-lys$^-$] began to appear at approximately pH 10. The ratio of [R-lys$^-$]/[R-lys$^+$] increased with an increase in the pH of the solution and reached a maximum value of 1.3 at pH 11 and then gradually decreased. This result shows the effect of Donnan membrane equilibrium on retaining the anion species in the resin phase starting from a solution pH greater than 10.

The selectivity coefficient of monovalent lysine against ammonium ion, $K^{\text{lys}^+}_{\text{NH}_4^+}$, was calculated by substitution of the experimental values of [R-lys] and [R-NH$_4^+$] in the solution into Eqs. (4)–(12), and the results were plotted against the solution pH, as shown in Fig. 6. The value of $K^{\text{lys}^+}_{\text{NH}_4^+}$ remained constant at 0.4 during the change of solution pH. This indicates that even in an alkaline pH range, the ion-exchange mechanism applied to the adsorption process can also be applied to the elution process when the Donnan membrane equilibrium effect is taken into account. Figure 7 shows a com-

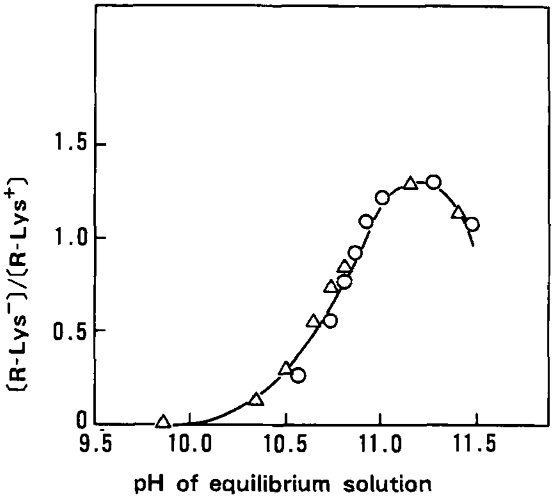

FIG. 5. The relationship between [R-lys$^-$]/[R-lys$^+$] and the equilibrium pH in equilibrium solution:

Adsorption pH	Symbol
1.8	△
4.0	○

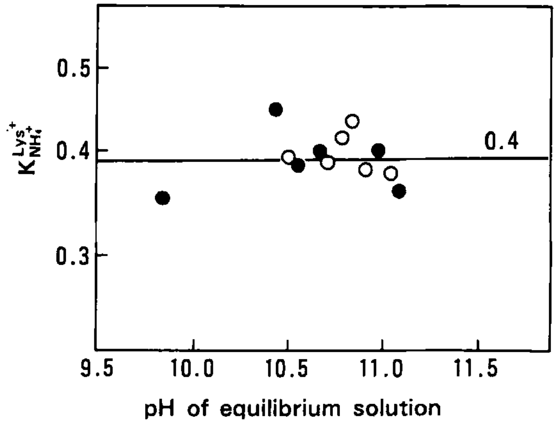

FIG. 6. The selectivity coefficient of monovalent lysine $K^{\mathrm{lys}^+}_{\mathrm{NH}_4^+}$ against pH of equilibrium solution:

pH in adsorption process	Symbol
1.8	●
4.0	○

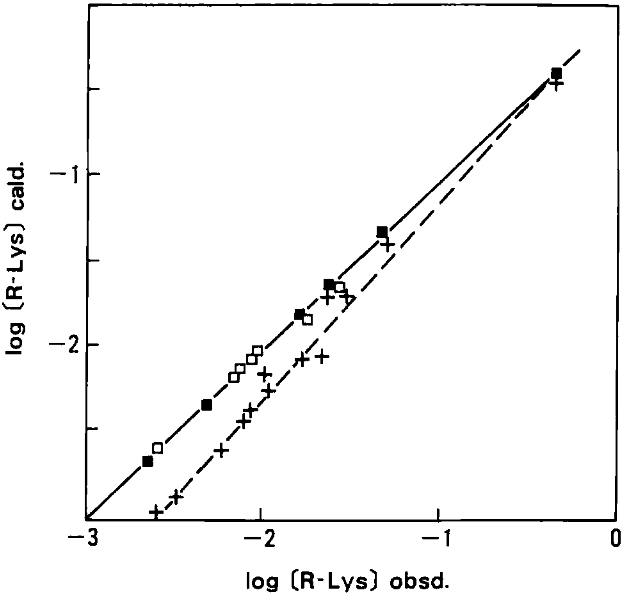

FIG. 7. Comparison of the calculated and the observed values of residual amount of lysine: (+) Calculated from ion-exchange equilibrium, (■, □) calculated from ion-exchange equilibrium with Donnan membrane equilibrium.

parison of calculated residual amounts of lysine based on Donnan membrane equilibrium with both the experimental values and calculated values based on ion-exchange equilibrium. The calculated values based on Donnan membrane equilibrium are in good agreement with experimental values with a regression coefficient of 0.99.

CONCLUSION

The elution mechanism of lysine adsorbed on a strong cation-exchange resin with ammonia water as the eluant was investigated by using the batch method. The behavior of the residual amount of lysine on the resin with changing equilibrium solution pH was found to be similar to that for the adsorption process at various equilibrium solution pHs. The selectivity coefficient of monovalent lysine changed with a change of equilibrium solution pH, whereas the selectivity coefficients of inorganic ionic species remained constant with a change in the solution pH: 1.13 for potassium ion and 0.91 for sodium ion. The elution mechanism of lysine in alkaline pH regions was examined while taking into account, the Donnan membrane equilibrium. The calculated value of the resin phase pH was found to be more acidic than that in the equilibrium solution, and the selectivity coefficient of monovalent lysine was found to have a constant value of 0.4. Simulation of the elution process by the batch method was performed with the proposed model, and it was shown to be in good agreement with the experimental data. This result shows that our elution model successfully verifies the elution mechanism in alkaline pH regions.

NOMENCLATURE

$(H^+)_S$	hydrogen concentration in solution (mol/L)
$K_{NH_4^+}^{A^+}$	selectivity coefficient of A-cation for ammonium form
k_1	first dissociation constant of lysine: 1.25×10^{-9}
k_2	second dissociation constant of lysine: 5.25×10^{-11}
k_a	dissociation constant of ammonia: 1.78×10^{-9}
K_w	dissociation constant of water: 1.0×10^{-14}
(X^-)	ion-exchange capacity of ammonium form resin (mol/L)
$[R\text{-}lys^+]$	residual amount of lysine on the resin (mol/L)
$[R\text{-}A^+]$	concentration of A-cation on the resin phase (mol/L)
Y^+	summation of cations on the resin phase
V_R	volume of resin (L)
V_S	volume of solution (L)
$(\ )_s$	concentration in solution (mol/L)

Subscripts

0	initial value
s	solution phase

REFERENCES

1. H. Maruyama, T. Matsuishi, and T. Kawakita, *Nippon Kagaku Kaishi, 50,* 253 (1976).
2. O. D. Bonner and L. L. Smith, *J. Phys. Chem., 61,* 326 (1957).
3. T. Kawakita, T. Ogura, and M. Saeki, *J. Agric. Biol. Chem., 53,* 2572 (1989).
4. F. G. Donnan, *Chem. Rev., 1,* 73 (1925).

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