아미노산의 다성분 이온교환 평형량예측

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Prediction of Multicomponent Ion Exchange Equilibria for Amino Acids

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INTRODUCTION

Amino acids, which are fundamental units making up proteins, have an important role in the pharmaceutical, food, and health product industries as intermediates. In the early days, the production of amino acids was based on recovery from protein hydrolysates. But presently they are produced by the microbial fermentation processes. It is separated from the fermentation broth by complicated and costly ion-exchange schemes due to low fermentation titer and very low solubility in organic media.

Ion-exchange resins are commonly used for the separation of amino acids both on analytical scale and in industrial manufacturing processes. Since amino acids which are called zwitterions exist both as anions and cations, depending upon the pH of the solution in which they are present, we can use various ion-exchange resins. In actual processes, amino acids are obtained by means of chromatographic techniques using ion-exchange resins. So it is necessary to investigate the accurate equilibria, kinetics, and dynamics in detail.

In this study we get the results on the exact equilibrium uptake of amino acids by an ion-exchange resin. An ion-exchange model that assumes the heterogeneity of the resin functional groups is used to fit binary exchange data and predict the equilibrium in multicomponent systems.

THEORY

Amino acids are amphoteric molecules with a structure that can be generally represented as $NH_2CHRCOOH$. The aqueous solution the following equilibrium dissociation reactions take place

$$NH_3^+ CHRCOOH\ (A_i^+) \longleftrightarrow NH_3^+ CHRCOO^-\ (A_i^\pm)\ +\ H^+ \qquad (1)$$
$$NH_3^+ CHRCOO^- \longleftrightarrow NH_2 CHRCOO^-\ (A_i^-)\ +\ H^+ \qquad (2)$$

The ionic fraction of the amino acid in solution is calculated as

$$X_{A_i} = [A_i^+] / [A_i^+] + [H^+] \qquad (3)$$

The exchange of an amino acid cation with hydrogen ion may be represented by the reaction

$$RH \; + \; A_i^+ \; = \; RA_i \; + \; H^+ \tag{4}$$
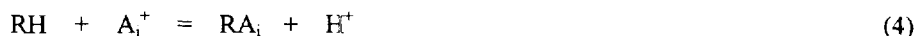
The ion-exchange equilibrium model is based on a binomial distribution of functional groups with arbitrary skewness.   Choosing counterion j as the reference ion, the selectivity coefficient for ion i relative to ion j is given by

$$S_{i,j} = \frac{Y_i X_j}{Y_j X_i} = \bar{S}_{i,j} \frac{\sum\limits_{k=1}^{N} \{ \bar{S}_{k,j} X_k W_{k,j}^{U+V} [(1-p) W_{i,k}^U + p W_{i,k}^V] \}}{\sum\limits_{k=1}^{N} \{ \bar{S}_{k,j} X_k W_{k,j}^{U+V} [(1-p) W_{j,k}^U + p W_{j,k}^V] \}} \tag{5}$$

where

$$U = \frac{-p}{\sqrt{p(1-p)}} \tag{6}$$

$$V = \frac{1-p}{\sqrt{p(1-p)}} \tag{7}$$

$\bar{S}$ represents an average selectivity coefficient for all ranges of ionic fractions from 0 to 1, W is the heterogeneity parameter that depends upon the variance of the distribution of selectivities among the functional groups, and p is the skewness of the binomial distribution of functional groups.   The resin-phase composition can be determined from $S_{i,j}$ values from the following equation:

$$Y_i = \frac{q_i}{q_0} = \frac{X_i S_{i,j}}{\sum\limits_{k=1}^{N} X_k S_{k,j}} \tag{8}$$

EXPERIMENTAL

Amberite 200 (Rohm & Haas Co.), the resin used in this study, is a macroreticular, sulfonated polystyrene resin.   The physical properties of this material are given in Table1. The total ion-exchange capacity of the resin, q_0, was determined by equilibrating a sample of the resin in the hydrogen form with an excess volume of 0.1 mol/L NaOH containing 50 g/L of sodium chloride.   At equilibrium, the excess NaOH was titrated with 0.1 mol/L HCl and the capacity determined from an material balance.   The resin capacity was found to be 4.26 mmol/g of dry resin.   The dry weight of fully swollen resin was obtained by determining the weight loss of a hydrated sample in the hydrogen form upon drying in an oven at 100 °C for 10 hours.

Prior to any experiments, the resin was pretreated by repeated washes with 1 mol/L HCl and 1 mol/L NaOH, converted to the desired ionic form, and then throughly rinsed with deionized distilled water.

The amino acids treated in this study were L-phenylalanine(Phe) and L-tyrosine(Tyr). Both amino acids were obtained in crystalline form from Sigma and used without further purification.   The ionization constants of amino acids used are given in Table 2.

The equilibrium uptake of amino acids was determined by means of batch equilibrium experiments.   For this purpose, varying amounts of ion-exchange resin (0.1- 0.2 g) in the hydrogen form were contacted with known volumes of standard solutions containing an

initial concentration of amino acids in sealed Erlenmeyer flasks.   The flasks were placed in a constant-temparature shaker bath kept at 25 °C for 72 hours.   Liquid samples were analyzed by UV spectrometry.   The pH of the solution after equilibrium was determined with a pH-selective probe.   The equilibrium concentration of amino acids in the resin phase were determined from material balances.

Table 1.   Physical   Properties   of   ion-exchange resin, Amberite 200

Property	Amount
Ion -exchange capacity (mol.kg)	4.26
Partical density (kg/m^3)	892(669)$^+$
Water content (%)	48-50
Degree of crosslinking * (%)	20
Average particle diameter ** (10^{-3}m)	0.80
Void fraction of micropore $^{++}$	0.29

* Manufacturer's specification
** 16/50 mesh,   mixed particles
$^+$ After swelling
$^{++}$ Yoshida et al.

Table 2.   Properties of amino acids used at 25°C

Property	Phe	Tyr
solubility in water (kg/m^3)	29.6	0.453
Molecular Weight	165.2	181.2
pK1	1.83	2.20
pK2	9.13	9.11
pK3	-	10.07
pI	5.48	5.65

RESULTS   AND   DISCUSSIONS

Figure 1. shows the various ionic distribution and ionic fraction of the amino acid cations, X_{Ai}, depending on the pH of aqueous solutions of phenylalanine.   The equilibrium uptake of Phe by Amberite 200 in the hydrogen form is shown in Figure 2.

For a given total concentration, the pH decreased with the Cl^- concentration.   It was also shown that the uptake of amino acid by the resin decreased, because of the competition with hydrogen ion for resin functional groups.   We have successfully used an exchange equilibrium model that accounts for the heterogeity of the resin in predicting multicomponent ion equilibrium.

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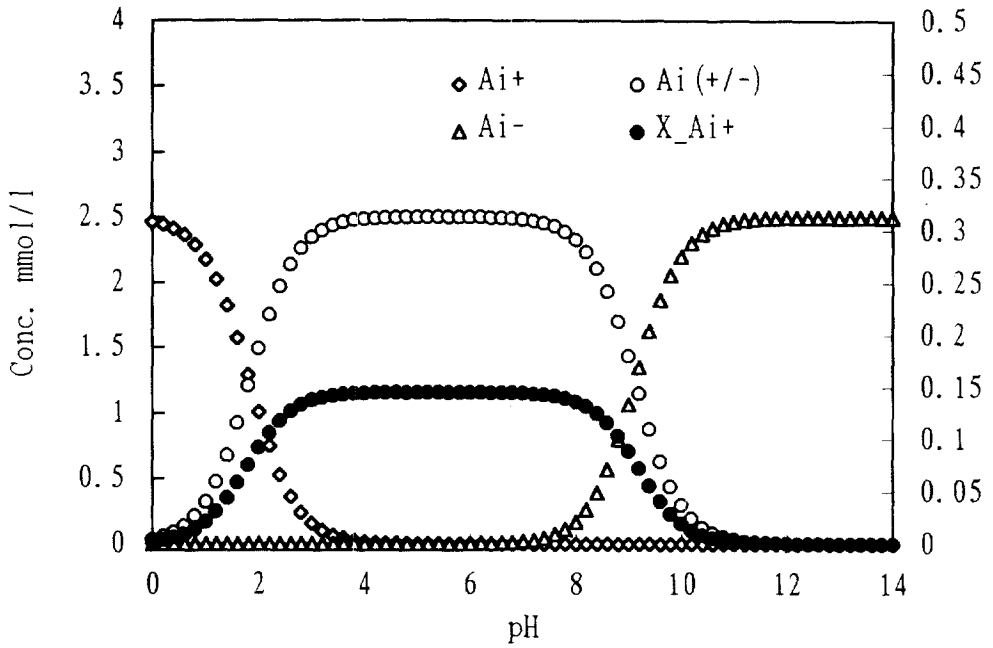
Figure 1. Ionic distribution and ionic fraction of amino acid cations, X_{Ai}, depending on the solution pH for phenylalanine.
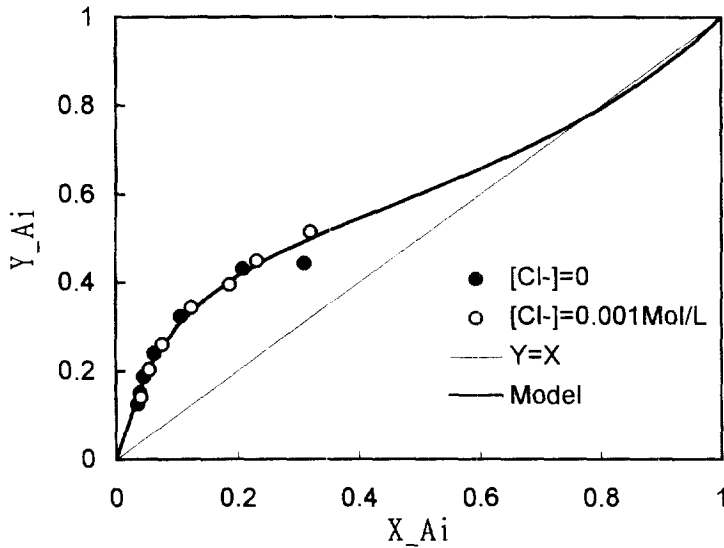

Figure 2. Ion-exchange equilibrium for Phe^+/H^+ binary system.