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Adsorption of Glutamic Acid on Crosslinked Chitosan Fiber: Equilibria

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ABSTRACT

Equilibria for adsorption of L-glutamic acid on the crosslinked chitosan fiber (ChF-B) which has one kind of fixed ammonium group were investigated theoretically and experimentally. Adsorption of L-glutamic acid on ChF-B appeared technically feasible. The experimental equilibrium isotherm was independent of the initial concentration of L-glutamic acid but depended on the pH of the solution significantly. The significant effect of the pH in the experimental equilibrium isotherm disappeared in plots of the equilibrium amount of L-glutamic acid in the adsorbent phase vs the concentration of the neutral L-glutamic acid in the liquid phase. This suggested that the adsorption of L-glutamic acid was controlled by the acid/base neutralization reaction between neutral L-glutamic acid and the fixed ammonium group of ChF-B. A Langmuir–Freundlich type of equation was derived based on the mass action law. It was assumed that L-glutamic acid was adsorbed by the acid/base neutralization reaction between the carboxylic group of the neutral L-glutamic acid and the fixed ammonium group of ChF-B. The association number of L-glutamic acid appeared to be 2. The experimental equilibrium isotherms for any constant pH and the effect of the pH on the equilibrium amount of L-glutamic acid adsorbed on ChF-B were correlated well by the theoretical equations.

INTRODUCTION

Ion exchangers have played important roles in the separation, purification, and recovery of amino acids. Since the net charge on these molecules varies in magnitude and sign when the pH of the solution changes, an

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amino acid is adsorbed on an ion exchanger or desorbed from it by controlling the pH of the solution. Therefore it is important to study the representation of the uptake equilibria of amino acids on ion-exchange resins as a function of the pH and the composition of the solution. Seno and Yamabe (1, 2) reported the way in which the pH of the solution affects the uptake equilibria of some amino acids. They assumed that the amino acids were adsorbed on strongly acidic or basic ion-exchange resins by the ion-exchange reaction and presented a theoretical equation for the equilibria on the basis of the mass action law. Haynes (3) described the role of the Donnan equilibrium in the ion exchange of several amino acids by the hydrogen form of a strong cation-exchange resin. Dye et al. (4) investigated the equilibria for adsorption of amino acids on a strong acid cation-exchange resin. They showed that the adsorption of an amino acid on the hydrogen form of the resin occurred primarily as the stoichiometric exchange of amino acid cations for hydrogen ion. Helfferich (5) derived equations for the equilibrium uptake of neutral, acidic, and basic amino acids by strong acid cation exchangers as a function of pH, concentrations of amino acid, and electrolyte or buffer added in the solution. DeCarli et al. (6) reported about the operation of a continuous displacement chromatograph for the separations of dilute mixtures of amino acids by using a strong acid cation-exchange resin.

The above investigations are mainly adsorption of the amino acids on strongly acidic or strongly basic ion exchangers. Few equilibrium isotherms for adsorption of an amino acid on weakly basic or weakly acidic ion exchangers have been reported. Yoshida and Kishimoto (7) investigated the adsorption of L-glutamic acid on a typical weakly basic ion exchanger that has one kind of the functional group (tertiary amino group) fixed in the resin phase. They assumed that the adsorption of L-glutamic acid was controlled by the acid/base neutralization reaction between undissociated carboxylic acid of the neutral L-glutamic acid and the ammonium group of a weakly basic ion exchanger, and presented theoretical equations of the equilibrium isotherm which correlated the experimental data reasonably well. Yoshida et al. (8) showed that polyaminated highly porous chitosan (hereafter called PEI-CH) (9) was technically feasible for adsorption of L-glutamic acid. PEI-CH is a kind of weakly basic ion exchanger which was fabricated by introducing poly(ethylene imine) into the macropore of highly porous crosslinked chitosan. PEI-CH has four different fixed amino groups: the primary amino group of chitosan and the primary, secondary, and tertiary amino group of poly(ethylene imine) fixed in the adsorbent particle. They assumed that the adsorption of L-glutamic acid was controlled by the acid/base neutralization reaction between undissociated carboxylic acid of the neutral L-glutamic acid and four different amino groups of PEI-CH, and presented theoretical equations of the equilibrium isotherm which correlated the experimental data reasonably well. In the above theoretical analysis for both resins, the association number of L-glutamic acid was assumed to be unity.

Yoshida et al. (10, 11) developed the crosslinked chitosan fiber and applied it to adsorption of direct dye and acid dye. They reported that the crosslinked chitosan fiber appeared technically and economically feasible for adsorption of those dyes. Since the crosslinked chitosan fiber has one kind of weakly basic functional group ($-NH_2$) in the adsorbent phase, it is a kind of weakly basic ion exchanger. In the present work we investigate not only the possibility of using the crosslinked chitosan fiber for adsorption of L-glutamic acid but also its adsorption mechanism.

The equilibrium isotherm and titration curve for the adsorption of HCl are presented to give the concentration of the functional group in the adsorbent phase and to show the properties of the functional group in the fiber. Theoretical equations for the equilibrium isotherm and the effect of the pH on the equilibrium amount of L-glutamic acid adsorbed on the crosslinked chitosan fiber (hereafter called the q_A–pH curve) are derived by assuming an acid/base neutralization reaction between neutral L-glutamic acid and a fixed amino group of the crosslinked chitosan fiber. They are compared with the experimental equilibrium isotherms and the q_A–pH curve. The theoretical and experimental results for the crosslinked chitosan fiber are discussed in relation to the results for a normal weakly basic ion exchanger (7).

EXPERIMENTAL

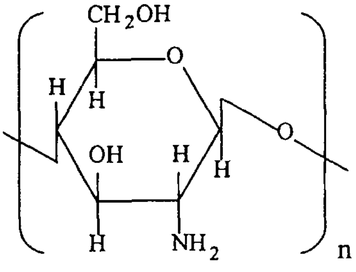
Materials

We used the crosslinked chitosan fiber (hereafter called ChF-B) in this experimental study. Figure 1 shows the unit molecular structure of chitosan. Chitin is a natural biopolymer which is contained in the shell of arthropods. The chitosan was transformed from chitin by deacetylation. Chitosan was crosslinked to make an adsorbent with acid, alkaline, and chemical proofs. The method of fabrication of ChF-B was presented elsewhere (10, 11).

The experimental physical properties of ChF-B are given in Table 1.

Procedures

Before measuring the equilibrium isotherms, ChF-B was packed in a column and was thoroughly washed with deionized distilled water at room temperature. Thereafter, ChF-B was dried at room temperature for 7 days



Chitosan

FIG. 1 Unit molecular structure of chitosan.

and then dried at 353 K for 3 hours. The dried ChF-B was kept in a desiccator.

L-Glutamic acid was a guaranteed reagent (Tokyo Kasei Co.). The equilibrium isotherms for adsorption of HCl and L-glutamic acid were measured by the batch method. Equilibrium was fully reached in 4 days. The pH of the L-glutamic acid solution was adjusted using HCl or NaOH. The L-glutamic acid solution was analyzed with a Shimadzu Liquid Chromatograph Model LC-3A and a Shimadzu Fluorescence HPLC Monitor Model RF-535. The pH of the equilibrium solution of L-glutamic acid was analyzed with a Horiba pH meter Model F-16. In addition, in the measurement of the equilibrium isotherm of HCl, when the concentration of HCl in the liquid phase was higher than 5 mol/m^3, HCl was analyzed by neutralization titration, and when it was lower than 5 mol/m^3, HCl was analyzed with a pH meter.

TABLE 1
Experimental Physical Properties of ChF-B

Concentration of amino groups fixed in adsorbent phase, Q (kmol/kg dry fiber)	3.32[a]
Water content (kg water/kg dry fiber)	1.14[b]
Density:	
True (kg/m^3)	1630[b]
Apparent (kg-dry fiber/m^3-wet fiber)	574[b]
Length (cut) (mm)	3–5[b]
Diameter (μm):	
Single fiber	20[b]
Apparent diameter (bundle of the fibers)	300[b]

[a] This work.

[b] Yoshida et al. (10, 11).

The adsorbent-phase concentration was calculated according to

$$q_i = \frac{(C_{0,i} - C_i)V}{W} \qquad (i = \mathrm{A, HCl}) \tag{1}$$

where $C_{0,i}$ and C_i are the initial concentration and equilibrium concentration in the liquid phase (kmol/m^3), respectively. q_i denotes the equilibrium concentration in the adsorbent phase (mol/kg of dry fiber). V and W are the volume of the solution (m^3) and the weight of the dry fiber (kg), respectively. The value of V/W (m^3 of solution/kg of dry fiber) was 0.0625 − 1. Since the volume of water which soaked in the dry fibers was smaller than 1.8% of the volume of the solution, the adsorbent-phase concentration was calculated according to Eq. (1) without correcting the value of V. Subscript A denotes L-glutamic acid.

All experiments were carried out at 298 K.

RESULTS

Equilibrium Isotherm of HCl

Figure 2 shows the experimental equilibrium isotherm for adsorption of HCl on ChF-B. The isotherm is very favorable. Since the equilibrium isotherm is independent of the initial concentration of HCl ($C_{0,\mathrm{HCl}}$), HCl may be adsorbed by the following acid/base neutralization reaction.

$$\mathrm{R{-}NH_2 + HCl} \overset{b_{\mathrm{HCl}}}{\rightleftharpoons} \mathrm{R{-}NH_3^+Cl^-} \tag{2}$$

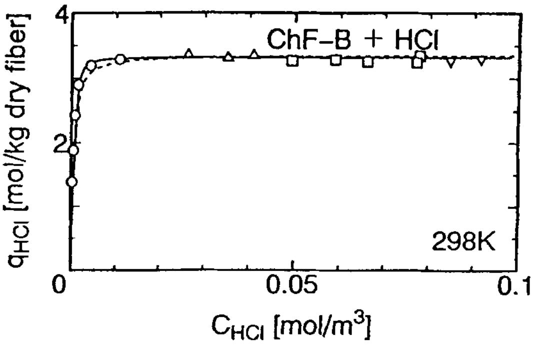


FIG. 2 Equilibrium isotherms for adsorption of HCl on ChF-B. (○) C_0 = 0.02 kmol/m^3, (△) C_0 = 0.05 kmol/m^3, (□) C_0 = 0.08 kmol/m^3, (▽) C_0 = 0.10 kmol/m^3. (- - -) Eq. (3); (——) Eq. (5).

where R—NH$_2$ denotes a fixed primary amine of a unit molecule of chitosan (see Fig. 1). Applying the mass action law to Eq. (2), the Langmuir equation (Eq. 3) is derived:

$$q_{\mathrm{HCl}} = \frac{Q_{\mathrm{HCl}} b_{\mathrm{HCl}} C_{\mathrm{HCl}}}{1 + b_{\mathrm{HCl}} C_{\mathrm{HCl}}} \tag{3}$$

The dashed line in Figure 2 shows the Langmuir isotherm. Equilibrium constant b_{HCl} and saturation capacity Q_{HCl} are listed in Table 2. The value of Q_{HCl} gives the concentration of the fixed ammonium group in the adsorbent phase. The values of b_{HCl} and Q_{HCl} were determined by the following equation to which Eq. (3) was transformed:

$$q_{\mathrm{HCl}} = Q_{\mathrm{HCl}} - \frac{1}{b_{\mathrm{HCl}}} \frac{q_{\mathrm{HCl}}}{C_{\mathrm{HCl}}} \tag{4}$$

The data were plotted based on Eq. (4), that is, q_{HCl} vs $q_{\mathrm{HCl}}/C_{\mathrm{HCl}}$. The data measured for three different $C_{0,\mathrm{HCl}}$ were correlated well by the straight line without scattering. The correlation coefficient was −0.934. When the absolute value of the correlation coefficient is larger than about 0.9, the straight line determined using the least square method has sufficient accuracy. The values of b_{HCl} and Q_{HCl} were determined from the intercept and slope of the straight line, respectively.

TABLE 2
Experimental Langmuir–Freundlich Coefficients for Adsorption of HCl and L-Glutamic Acid on ChF-B

	i	Q_i (mol/kg)	m_i	b_i (kmol/m^3)	Q_i/Q_{HCl}	Correlation coefficients	Figure
ChF-B:							
	HCl	3.33	1	6.41×10^3		−0.934	2, 3
	HCl	3.32 (Q_{HCl})	1.58	2.44×10^3		0.999	2, 3
	A	2.32	2.17	2.14×10^2	0.699	0.999	4
	$A^{\pm}$	2.33	2	2.62×10^2	0.702	0.915	8[a]
WA30:[b]							
	$A^{\pm}$	2.20	1	4.98×10^2	0.705		

[a] The data include all of Fig. 4, the data with NaOH shown by closed keys in Fig. 5, and all of Fig. 6 which were obtained without HCl.

[b] Yoshida and Kishimoto (7).

Titration Curve

In order to understand the adsorption mechanism of L-glutamic acid on ChF-B clearly, especially when HCl exists in the solution, reliable equilibrium data for the adsorption of HCl are necessary. The values of b_{HCl} and Q_{HCl} were checked by measuring the titration curve of HCl over a wide range of pH. In Fig. 3 the equilibrium amount of HCl adsorbed is plotted versus the equilibrium value of pH in the solution (open circle). The data shown in Fig. 2 were also plotted using closed circles. Although the data in Fig. 3 were not obtained by the titration method but by the batch method for many different initial concentrations of HCl, these types of plots may be considered to be titration curves and have been considered an excellent means for studying ion exchange or adsorption characteristics (12, 13). The dashed line shows the Langmuir isotherm calculated from Eq. (3) using the Langmuir coefficients in Table 2. The data deviate from the dashed line when $2 < \mathrm{pH} < 3$ and $\mathrm{pH} > 3.7$. The solid line shows the Langmuir–Freundlich isotherm (14) (Eq. 5) using the values of Q_{HCl}, b_{HCl}, and m_{HCl} given in Table 2.

$$q_i = \frac{Q_i(b_iC_i)^{m_i}}{1 + (b_iC_i)^{m_i}} \tag{5}$$

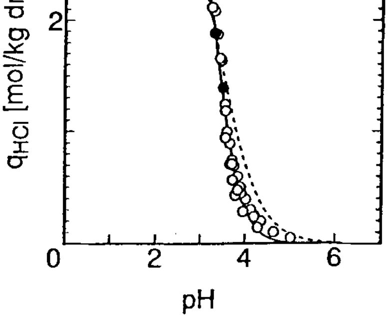


FIG. 3 Titration curve for adsorption of HCl on ChF-B. (- - -) Eq. (3); (——) Eq. (5).

The Langmuir–Freundlich coefficients were determined by the modified Marquardt method (15) using all experimental data. The data are correlated by the Langmuir–Freundlich equation, Eq. (5), much better than by the Langmuir equation. The correlation coefficient based on Eq. (A1) (see Appendix) was 0.999. From the above results, the value of Q_{HCl} determined using Eq. (5) may give the concentration of the fixed ammonium group in the adsorbent phase.

Equilibrium Isotherm of L-Glutamic Acid

Figure 4 shows the experimental equilibrium isotherm for adsorption of L-glutamic acid on ChF-B for the case with no electrolyte except for L-glutamic acid in the solution. The isotherm was measured for three different initial concentrations of L-glutamic acid ($C_{0,\mathrm{A}}$). Since the experimental equilibrium isotherm is independent of $C_{0,\mathrm{A}}$, L-glutamic acid may be adsorbed by chemisorption. The experimental equilibrium isotherm belongs to Type V in which intermolecular attraction effects are large (16). The solid line shows the Langmuir–Freundlich isotherm and correlates the data well (see the correlation coefficient in Table 2). The Langmuir–Freundlich coefficients Q_A, b_A, and m_A are listed in Table 2. They were determined by the modified Marquardt method (15) using all experimental data in Fig. 4. Saturation capacity Q_A is smaller than the concentration of the fixed amino group in the fiber Q_{HCl} as shown in Table 2. This will be discussed in the Theoretical Section.

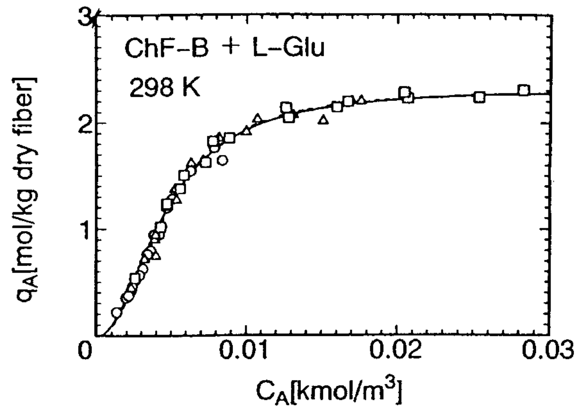


FIG. 4 Equilibrium isotherms for adsorption of L-glutamic acid on ChF-B for the case that there existed no electrolyte except for L-glutamic acid in the solution. (○) $C_0 = 0.01$ kmol/m^3, (△) $C_0 = 0.02$ kmol/m^3, (□) $C_0 = 0.03$ kmol/m^3. (——) Eq. (5) (i = A); (- - -) Eqs. (18) and (22).

Figure 5 shows the effect of pH on the equilibrium amount of L-glutamic acid in the adsorbent phase. The data were obtained by the batch method. The volume of the solution V was 1×10^{-5} m^3, the weight of the fiber W was 2×10^{-5} kg of dry fiber, and the initial concentration of L-glutamic acid $C_{0,A}$ was 10 mol/m^3 for each datum. The initial value of pH of each solution was adjusted using HCl or NaOH. The pH value of each datum in the figure was the final equilibrium value. Only when $2 < \text{pH} < 7$ is L-glutamic acid adsorbed on ChF-B. The q_A–pH curve shows a peak when the pH of the solution is about the isoelectric point of L-glutamic acid [pI = 3.22 (19)].

As the q_A–pH curve of ChF-B is sharp, the separation process for which L-glutamic acid is adsorbed at pH ≅ pI and is desorbed at pH < 2 or pH > 7 may be technically feasible.

In order to make clear the effect of pH on the adsorption of L-glutamic acid, we measured the equilibrium isotherms at different constant pH values (within ±0.1), and the results are given in Fig. 6. The pH values were adjusted by using NaOH. Since the q_A–pH curve for pH < 3.7 is very sharp, as shown in Fig. 5, and it was impossible to maintain pH constant when pH < 3.7, we could not obtain the equilibrium isotherms

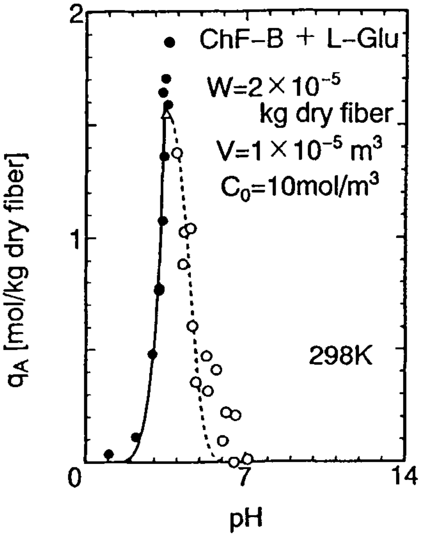


FIG. 5 Effect of pH on the equilibrium amount of L-glutamic acid adsorbed on ChF-B. (●) with HCl system, (○) with NaOH system, (△) without inorganic electrolyte. (——) Theoretical line calculated from Eqs. (23), (26), and (28); (- - -) theoretical line calculated from Eqs. (22) and (26).

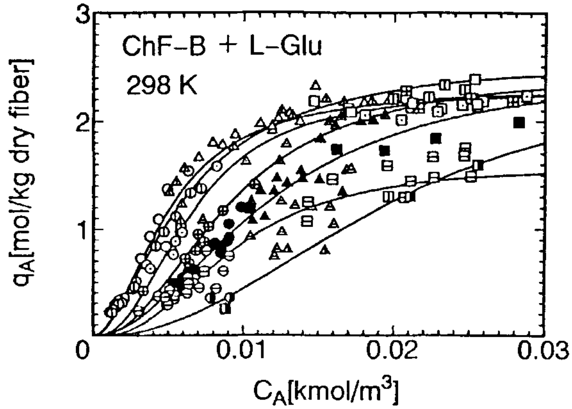


FIG. 6 Equilibrium isotherms for adsorption of L-glutamic acid on ChF-B at constant pH which was adjusted using NaOH. (○, △, □) pH 3.7; (⦶, △, ◫) pH 3.9; (⊙, △, ⊡) pH 4.1; (⊕, △, ⊞) pH 4.3; (●, ▲, ■) pH 4.5; (⊖, △, ⊟) pH 4.7; (◑, ▲, ◨) pH 4.9; (○, ⦶, ⊙, ⊕, ●, ⊖, ◑) C_0 = 0.01 kmol/m^3; (△, △, △, △, ▲, △, ▲) C_0 = 0.02 kmol/m^3; (□, ◫, ⊡, ⊞, ■, ⊟, ◨) C_0 = 0.03 kmol/m^3; (——) Eq. (5).

TABLE 3

Experimental Langmuir–Freundlich Equilibrium Coefficients for L-Glutamic Acid on ChF-B for the Data of q_A–C_A Curve at Different Constant pH (Fig. 6), Which Were Determined by the Modified Marquardt Method

i	pH	Q_i (mol/kg)	m_i	b_i (kmol/m^3)	Correlation coefficients
A	3.7	2.32	1.92	2.02×10^2	0.999
	3.9	2.59	1.69	1.63×10^2	0.996
	4.1	2.30	2.31	1.52×10^2	0.998
	4.3	2.47	2.19	1.10×10^2	0.997
	4.5	2.53	1.98	8.49×10^1	0.982
	4.7	1.60	2.49	1.07×10^2	0.986
	4.9	2.55	2.23	4.94×10^1	0.948
	Mean	2.44	2.12	—	—

for constant pH in that pH region. The isotherm is independent of the initial concentration of L-glutamic acid but depends on the pH value significantly. The amount of L-glutamic acid adsorbed on ChF-B is the largest at pH $\cong$ 3.7 and decreases with increasing pH. Since all experimental equilibrium isotherms belonged to Type V, they were matched with the Langmuir–Freundlich equation, Eq. (5). The Langmuir–Freundlich coefficients Q_A, b_A, and m_A for each pH value were determined by the modified Marquardt method (15), and they are given in Table 3. The solid lines in Fig. 6 show the Langmuir–Freundlich isotherms calculated using the coefficients in Table 3. The correlation coefficients based on Eq. (A1) are listed in Table 3.

EQUILIBRIUM THEORY

The following conclusions were obtained from the above experimental study: 1) The q_A–pH curve showed that L-glutamic acid was adsorbed only the region in $2 < \text{pH} < 7$ and the peak appeared around pH = pI. 2) The experimental equilibrium isotherms belonged to Type V and were correlated by the Langmuir–Freundlich equation. 3) The experimental equilibrium isotherms were independent of the initial concentration of L-glutamic acid but depended on pH significantly. 4) The values of Q_i were almost constant but b_i decreased with increasing pH. The mean value of Q_i was about 74% of the concentration of the fixed amino group of ChF-B.

In order to understand the above complicated results and to estimate equilibrium isotherms in any conditions, a theoretical analysis is necessary.

ChF-B is a weakly basic ion exchanger because the primary ammonium group of chitosan, which acts as the fixed functional group in the fiber, is weakly basic. Since the primary ammonium group does not have OH^- in the acid region, the maximum of the uptake in Fig. 5 may not be explained by the ion exchange between OH^- and negatively charged glutamic acid. As the experimental equilibrium isotherms for adsorption of L-glutamic acid on ChF-B were independent of the initial concentration in the liquid phase, L-glutamic acid may be adsorbed on ChF-B by chemisorption.

L-Glutamic acid dissociates as follows:

$$\text{Ra—NH}_3^+(\text{—COOH})_2 \overset{K_1}{\rightleftharpoons} \text{Ra—NH}_3^+(\text{—COO}^-)(\text{—COOH}) + \text{H}^+ \tag{6}$$

$$\mathrm{Ra{-}NH_3^+(-COO^-)(-COOH)} \overset{K_2}{\rightleftharpoons} \mathrm{Ra{-}NH_3^+(-COO^-)_2} + \mathrm{H^+} \tag{7}$$

$$\mathrm{Ra{-}NH_3^+(-COO^-)_2} \overset{K_3}{\rightleftharpoons} \mathrm{Ra{-}NH_2(-COO^-)_2} + \mathrm{H^+} \tag{8}$$

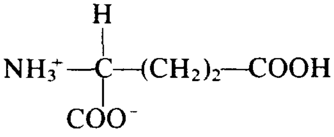
The equilibrium relations for Eqs. (6)–(8) are given by Eqs. (9)–(11), respectively.

$$K_1 = \frac{C_{A^\pm} C_{H^+}}{C_{A^-}} \tag{9}$$

$$K_2 = \frac{C_{A^-} C_{H^+}}{C_{A^\pm}} \tag{10}$$

$$K_3 = \frac{C_{A^{2-}} C_{H^+}}{C_{A^-}} \tag{11}$$

where A^+, $A^\pm$, A^-, and A^{2-} are the L-glutamic acid of $\mathrm{Ra{-}NH_3^+(-COOH)_2}$, $\mathrm{Ra{-}NH_3^+(-COO^-)(-COOH)}$, $\mathrm{Ra{-}NH_3^+(-COO^-)_2}$, and $\mathrm{Ra{-}NH_2(-COO^-)_2}$, respectively. Ra denotes the carbon chain of L-glutamic acid. For example,



$$\mathrm{NH_3^+{-}\underset{\displaystyle COO^-}{\overset{\displaystyle H}{C}}{-}(CH_2)_2{-}COOH}$$

is expressed by $\mathrm{Ra{-}NH_3^+(-COO^-)(-COOH)}$. Figure 7 shows the theoretical concentration distributions of A^+, $A^\pm$, A^-, and A^{2-} of L-glutamic acid in the liquid phase calculated from Eqs. (9)–(11) by using $K_1 = 6.46 \times 10^{-3}$ kmol/m^3, $K_2 = 5.62 \times 10^{-5}$ kmol/m^3, and $K_3 = 2.14 \times 10^{-10}$ kmol/m^3 (17). The distribution curve of $A^\pm$ is similar to the experimental q_A–pH curve in Fig. 5.

Assuming that m molecules of adsorbate B are adsorbed on one fixed functional group (R—X), the adsorption reaction is expressed by

$$\mathrm{R{-}X} + m\mathrm{B} \overset{K}{\rightleftharpoons} \mathrm{R{-}X{\cdot}B}^m \tag{12}$$

Applying the mass action law to Eq. (12), the equilibrium relation is given by

$$q = \frac{QKC^m}{1 + KC^m} \tag{13}$$

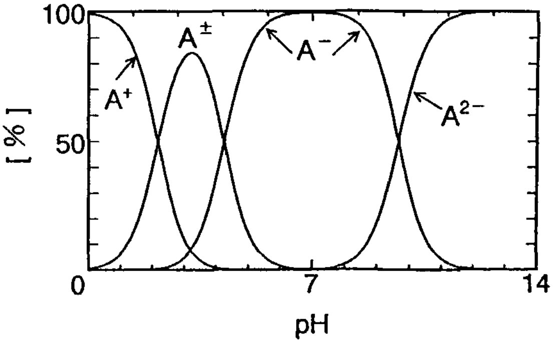


FIG. 7 Theoretical concentration distributions of L-glutamic acid in the liquid phase.

Substituting Eq. (14) into Eq. (13), the Langmuir–Freundlich equation (Eq. 15) is obtained.

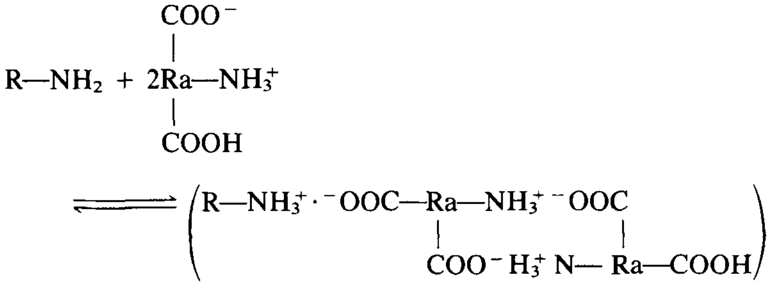
$$K = b^m \tag{14}$$

$$q = \frac{Q(bC)^m}{1 + (bC)^m} \tag{15}$$

where Q, b, and m show the saturation capacity, equilibrium constant, and association number of adsorbate B (the intermolecular attraction effect), respectively. Equations (12)–(15) may give the theoretical background of the Langmuir–Freundlich equation based on the mass action law.

For the experimental equilibrium isotherms for L-glutamic acid on ChF-B at different constant pH, the mean value of m_A is 2.12 as shown in Table 3. Since the value of m_A shows the intermolecular attraction effect (association number of L-glutamic acid), we assumed that two molecules of neutral L-glutamic acid ($A^\pm$) associated and were adsorbed by chemisorption on one fixed amino group of chitosan.

From the above discussion, L-glutamic acid may be adsorbed on ChF-B according to the following acid/base neutralization reaction:



$$R{-}NH_2 + 2\,\overset{COO^-}{\underset{COOH}{Ra{-}NH_3^+}} \rightleftharpoons \left(\begin{array}{l} R{-}NH_3^+\cdot{}^-OOC{-}Ra{-}NH_3^+\,{}^-OOC \\ \qquad\qquad\quad COO^-\,H_3^+N{-}\,Ra{-}COOH \end{array}\right) \tag{16}$$

Equation (16) is simply written as

$$\mathrm{R{-}NH_2} + 2\mathrm{A}^{\pm} \overset{K_{\mathrm{A}^{\pm}}}{\rightleftharpoons} \mathrm{R{-}NH_3^+\,(A^-A^{\pm})} \tag{17}$$

The concentration of $A^{\pm}$ in the liquid phase, $C_{A^{\pm}}$ (kmol/m^3) is given by Eq. (18).

$$C_{A^{\pm}} = \frac{C_A}{1 + \dfrac{C_{H^+}}{K_1} + \dfrac{K_2}{C_{H^+}} + \dfrac{K_2K_3}{C_{H^+}^2}} \tag{18}$$

$$C_A = C_{A^+} + C_{A^{\pm}} + C_{A^-} + C_{A^{2-}} \tag{19}$$

Equation (16) or (17) implies that the equilibrium isotherm for adsorption of L-glutamic acid on a ChF-B is given by an equation in which q_A is expressed by only one independent variable $C_{A^{\pm}}$.

System without HCl

In Fig. 8 the values of q_A are plotted versus $C_{A^{\pm}}$. The data include all of Fig. 4, the data with NaOH shown by closed keys in Fig. 5, and all of Fig. 6 which were obtained without HCl. The significant effect of pH in the q_A–C_A plots in Fig. 6 disappears in the q_A–$C_{A^{\pm}}$ plots in Fig. 8. In addition, we also plotted q_A vs C_{A^+}, q_A vs C_{A^-}, and q_A vs $C_{A^{2-}}$ using the same data as the ones in Fig. 8, respectively, but the plots were very

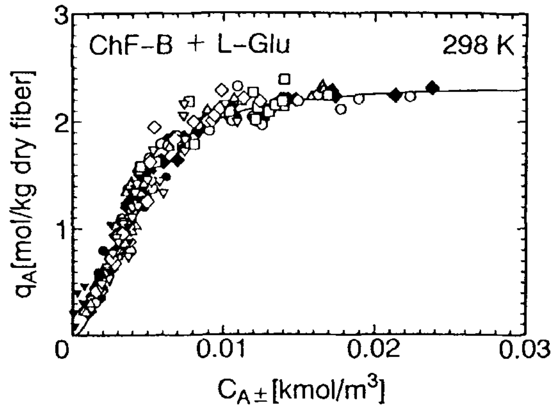


FIG. 8 Relation between q_A and $C_{A^{\pm}}$ for ChF-B without HCl system. (○) pH 3.7, (△) pH 3.9, (□) pH 4.1, (◇) pH 4.3, (▽) pH 4.5, (●) pH 4.7, (▲) pH 4.9, (◆) pure (Fig. 4), (▼) the data without HCl system in Fig. 5, (——) Eq. (22).

scattered. These results suggest that the adsorption reaction, Eq. (17), may be acceptable.

Applying the mass action law to Eq. (17), the equilibrium relation is given as follow:

$$q_A = \frac{Q_{A^\pm} K_{A^\pm} C_{A^\pm}^2}{1 + K_{A^\pm} C_{A^\pm}^2} \tag{20}$$

Substituting Eq. (21) into Eq. (20), the Langmuir–Freundlich type equation (Eq. 22) was obtained.

$$K_{A^\pm} = b_{A^\pm}^2 \tag{21}$$

$$q_A = \frac{Q_{A^\pm}(b_{A^\pm} C_{A^\pm})^2}{1 + (b_{A^\pm} C_{A^\pm})^2} \tag{22}$$

The values of $Q_{A^\pm}$ and $b_{A^\pm}$ for the q_A–$C_{A^\pm}$ curve were determined by modified Marquardt method and they are listed in Table 2. The solid line in Fig. 8 shows the theoretical line calculated from Eq. (22) using the values of $Q_{A^\pm}$ and $b_{A^\pm}$ in Table 2 and correlates well with the data (the correlation coefficient is 0.915). As shown in Table 2, the association number m for adsorption of L-glutamic acid on DIAION WA30 was unity (7). The intermolecular attraction effect was not observed as in ChF-B. This may be because the pore size of DIAION WA30 is smaller than that of ChF-B; in DIAION WA30, Reaction (16) cannot occur.

The dashed line in Fig. 4 shows the theoretical line calculated from Eqs. (18) and (22) using the value of $Q_{A^\pm}$ and $b_{A^\pm}$ given in Table 2; it is close to the solid line. The values of $Q_{A^\pm}$, $b_{A^\pm}$, and $m_{A^\pm}$ are close to Q_A, b_A, and m_A, respectively, for the data for the case in which no electrolyte for L-glutamic acid exists in the solution. The solid lines in Fig. 9, in which the same data as in Fig. 6 are plotted, represent the theoretical lines calculated from Eqs. (18), (19) and (22) using the values of $Q_{A^\pm}$ and $b_{A^\pm}$ given in Table 2. The experimental isotherm correlates well with the solid line for each constant pH.

In addition, we tried to correlate the data using the BET equation, the Radke–Prausnitz equation (18), the generalized Freundlich equation (19, 20), and the Toth equation (21). However, the data could not be correlated by these equations.

System with HCl

When HCl exists in an aqueous solution of L-glutamic acid, L-glutamic acid and HCl are adsorbed on each functional group of ChF-B by a simultaneous acid/base neutralization reaction. Since $Q_{A^\pm} < Q_{HCl}$, we assumed

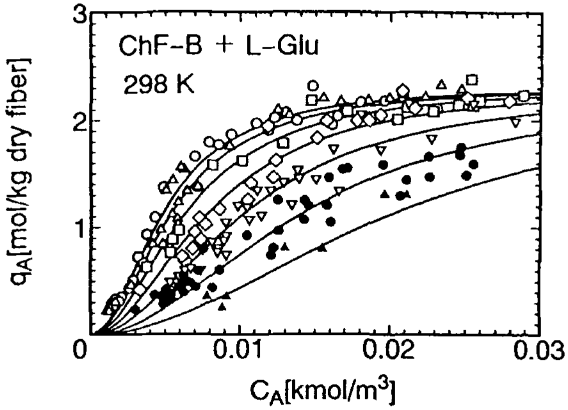


FIG. 9 Comparison of the data in Fig. 6 with the theoretical lines calculated from Eqs. (18) and (22). (○) pH 3.7, (△) pH 3.9, (□) pH 4.1, (◇) pH 4.3, (▽) pH 4.5, (●) pH 4.7, (▲) pH 4.9, (——) Eqs. (18) and (22).

that 1) HCl is adsorbed on all fixed amino groups (Q_{HCl}) and 2) L-glutamic acid is adsorbed on the amino groups fixed on the network and of large size ($Q_{\mathrm{A}^\pm}$) but cannot be adsorbed on the amino groups fixed on the network but of small size ($Q_{\mathrm{HCl}} - Q_{\mathrm{A}^\pm}$). In addition, Jones and Carta (22) investigated the ion exchange of some amino acids (alanine, leucine, and phenylalanine) and dipeptides (phenylalanylalanine and phenylalanylphenylalanine) on sulfonated polystyrene–divinylbenzene cation ion-exchange resins with a degree of crosslinking from 4 to 10%. They reported that the maximum uptake of amino acid was considerably lower than the resin ion exchange capacity as the solute size and the degree of crosslinking of the resin were increased. Combining Eqs. (5) and (22) based on the above assumptions, the equilibrium solid phase concentrations of L-glutamic acid and HCl are given by Eqs. (23) and (24), respectively.

$$q_{\mathrm{A}} = \frac{Q_{\mathrm{A}^\pm}(b_{\mathrm{A}^\pm}C_{\mathrm{A}^\pm})^{m_{\mathrm{A}^\pm}}}{1 + (b_{\mathrm{A}^\pm}C_{\mathrm{A}^\pm})^{m_{\mathrm{A}^\pm}} + (b_{\mathrm{HCl}}C_{\mathrm{HCl}})^{m_{\mathrm{HCl}}}} \qquad (23)$$

$$q_{\mathrm{HCl}} = \frac{Q_{\mathrm{A}^\pm}(b_{\mathrm{HCl}}C_{\mathrm{HCl}})^{m_{\mathrm{HCl}}}}{1 + (b_{\mathrm{A}^\pm}C_{\mathrm{A}^\pm})^{m_{\mathrm{A}^\pm}} + (b_{\mathrm{HCl}}C_{\mathrm{HCl}})^{m_{\mathrm{HCl}}}} + \frac{(Q_{\mathrm{HCl}} - Q_{\mathrm{A}^\pm})(b_{\mathrm{HCl}}C_{\mathrm{HCl}})^{m_{\mathrm{HCl}}}}{1 + (b_{\mathrm{HCl}}C_{\mathrm{HCl}})^{m_{\mathrm{HCl}}}} \qquad (24)$$

As all equilibrium coefficients Q_{HCl}, $Q_{\mathrm{A}^\pm}$, b_{HCl}, $b_{\mathrm{A}^\pm}$, $m_{\mathrm{A}^\pm}$, and m_{HCl} are known now (Table 2), a theoretical equilibrium isotherms can be calculated from Eqs. (23) and (24) when HCl exists in the solution. Equation (23) should be tested by comparing experimental equilibrium isotherms for constant pH. However, the experimental isotherm at constant pH for the adsorption of L-glutamic acid with HCl could not be obtained because it was difficult to maintain a constant solution pH. Therefore, the theoretical q_A–pH curve was calculated using Eq. (23) and it was compared with the experimental q_A–pH curve with HCl in the system (Fig. 5). Equation (22) was also tested by comparing it with the experimental q_A–pH curve without HCl in the system (Fig. 5).

Theoretical q_A–pH Curve

Theoretical q_A–pH curves with HCl in the system and without HCl in the system were calculated using Eqs. (23) and (22), respectively.

The experimental adsorbed phase concentrations of L-glutamic acid given in Fig. 5 were calculated according to Eq. (1). Equation (1) is transformed to

$$C_A = C_0 - q_A \frac{W}{V} \tag{25}$$

By substituting Eq. (25) into Eq. (18), Eq. (26) is obtained:

$$C_{A^\pm} = \frac{C_0 - q_A \dfrac{W}{V}}{1 + \dfrac{C_{H^+}}{K_1} + \dfrac{K_2}{C_{H^+}} + \dfrac{K_2 K_3}{C_{H^+}^2}} \tag{26}$$

When HCl exists in the solution, it is necessary to consider the concentration of HCl. The condition of electroneutrality is given by

$$C_{H^+} + C_{A^+} = C_{A^-} + 2C_{A^{2-}} + C_{OH^-} + C_{Cl^-} \tag{27}$$

When $C_{Cl^-} < C_{H^+}$, C_{HCl} is calculated from Eq. (28) which is derived from Eqs. (9)–(11) and (27):

$$C_{HCl} = C_{Cl^-} = C_{H^+} - \frac{K_W}{C_{H^+}} + \left(\frac{C_{H^+}}{K_1} - \frac{K_2}{C_{H^+}} - \frac{2K_2K_3}{C_{H^+}^2}\right) C_{A^\pm} \tag{28}$$

When $C_{Cl^-} > C_{H^+}$, C_{HCl} is equal to C_{H^+}.

The solid line in Fig. 5 was the theoretical line (with HCl) calculated from Eqs. (23), (26), and (28). The values of $Q_{A^\pm}$, $b_{A^\pm}$, b_{HCl}, $m_{A^\pm}$, and m_{HCl} in Eq. (23) are given in Table 2. C_0, W, and V in Eq. (26) were 10 mol/m^3, 2×10^{-5} kg, and 1×10^{-5} m^3, respectively. A value of q_A was assumed for a given value of C_{H^+}. The value of $C_{A^\pm}$ was calculated from

Eq. (26) using the C_{H^+} value and the assumed value of q_A. Thereafter, the value of C_{HCl} was calculated from Eq. (28) when $C_{Cl^-} < C_{H^+}$. When $C_{Cl^-} > C_{H^+}$, it was equal to C_{H^+}. Substituting the value of $C_{A^\pm}$ and C_{HCl} into Eq. (23), the new value of q'_A was obtained. When the relative error of the value of q'_A for the assumed value of q_A was smaller than 10^{-6}, the value of q'_A gave the solution of Eqs. (23), (26), and (28). If the relative error was larger than 10^{-6}, a new value of q_A was set as $(q_A + q'_A)/2$, and the above calculation was repeated until the relative error came within 10^{-6}. The solid line agrees reasonably well with the experimental q_A–pH curve for the system with HCl and pH < 3.7.

When the pH of the solution is adjusted using NaOH or when there are no inorganic electrolytes in the solution, only L-glutamic acid is adsorbed on ChF-B. The dashed line in Fig. 5 is a theoretical line (without HCl in the system) calculated from Eqs. (22) and (26). Equilibrium coefficients $Q_{A^\pm}$ and $b_{A^\pm}$ in Eq. (22) are given in Table 2. A value of q_A was assumed for a given value of C_{H^+}. The value of $C_{A^\pm}$ was calculated from Eq. (26) using the C_{H^+} value and the assumed q_A. Substituting the value of $C_{A^\pm}$ into Eq. (22), the new value of q'_A was obtained. When the relative error of the value of q'_A for the assumed value of q_A was smaller than 10^{-6}, the value of q'_A gave the solution of Eqs. (22) and (26). If the relative error was larger than 10^{-6}, the value of q_A was set as $(q_A + q'_A)/2$, and the above calculation was repeated until the relative error came within 10^{-6}. The dashed line agrees reasonably well with the experimental q_A–pH curve for the system without HCl and pH > 3.7.

Yoshida and Kishimoto (7) investigated the adsorption of L-glutamic acid on the commercial weakly basic ion-exchanger DIAION WA30 which has one kind of fixed ammonium group. They did not observed the intermolecular attraction effect seen with ChF-B. The difference in the equilibrium behaviors of L-glutamic acid with ChF-B and with DIAION WA30 is not clear.

CONCLUSION

The adsorption of L-glutamic acid on a crosslinked chitosan fiber (ChF-B) appeared technically feasible. An equilibrium theory for the adsorption of L-glutamic acid on ChF-B, which has one kind of primary amino group, was proposed. The experimental equilibrium isotherms and the q_A–pH curve for the adsorption of L-glutamic acid on ChF-B were presented and the following conclusions were obtained.

1. The experimental equilibrium isotherm for the adsorption of L-glutamic acid on ChF-B was independent of the initial concentration of L-glutamic acid but depended significantly on the pH of the solution.

2. The significant effect of pH in q_A–C_A plots disappeared in q_A–$C_{\mathrm{A}^\pm}$ plots. This suggested that L-glutamic acid was not adsorbed by stoichiometric ion exchange but by the acid/base neutralization reaction between the $\mathrm{A}^\pm$ type of L-glutamic acid and the weakly basic functional groups in ChF-B.
3. The Langmuir–Freundlich equation (Eq. 15) could be derived by applying the simple mass action law to Eq. (12). It appeared that the Langmuir–Freundlich coefficient m showed the association number of the adsorbate (the intermolecular attraction effect). In the adsorption of L-glutamic acid on ChF-B, the association number was 2 (Eq. 16).
4. When HCl was not in the solution, the theoretical isotherm was given by a Langmuir–Freundlich type equation, Eq. (22). When HCl was in the solution, the theoretical equation was expressed by Eq. (23). The isotherms (q_A–C_A curves) for any constant pH value were determined reasonably well by Eqs. (18), and (22) or (23). The q_A–pH curves were obtained reasonably well by the theoretical equations (Eqs. 22 or 23 and 26).

APPENDIX

The accuracy of the Langmuir–Freundlich coefficients which were determined by the modified Marquardt method (15) was checked by using all the experimental data as follows. Equation (5) was transformed to

$$C_i^{m_i} = -\frac{1}{b_i^{m_i}} + Q_i\frac{C_i^{m_i}}{q_i} \qquad (i = \mathrm{A}, \mathrm{A}^{\pm}) \tag{A1}$$

Using m_i as determined by the modified Marquardt method (15), plots of the experimental data between $C_i^{m_i}$ and $C_i^{m_i}/q_i$ were in a straight line. The values of b_i and Q_i determined from the intercept and the slope of Eq. (A1) were close to the values of b_i and Q_i determined by the modified Marquardt method (15). To estimate the scattering of the data from a straight line, we introduced the correlation coefficient. If plots of the data between $C_i^{m_i}$ and $C_i^{m_i}/q_i$ are in a straight line, then the absolute value of the correlation coefficient $|r|$ should approach unity. When $|r| > 0.9$, the Langmuir–Freundlich coefficients b_i, m_i, and Q_i are valid. The calculated correlation coefficients r are given in Tables 2 and 3.

NOMENCLATURE

b_i	equilibrium constant for Langmuir–Freundlich equation
$C_{0,\mathrm{A}}$	initial concentration of L-glutamic acid in liquid phase (kmol/m^3)

$C_{0,\mathrm{HCl}}$	initial concentration of HCl in liquid phase (kmol/m^3)
C_{HCl}	equilibrium concentration of HCl in liquid phase (kmol/m^3)
C_{A}	equilibrium concentration of L-glutamic acid in liquid phase (kmol/m^3)
C_{A^+}	equilibrium concentration of A^+ type of L-glutamic acid in liquid phase (kmol/m^3)
$C_{\mathrm{A}^\pm}$	equilibrium concentration of $\mathrm{A}^\pm$ type of L-glutamic acid in liquid phase (kmol/m^3)
C_{A^-}	equilibrium concentration of A^- type of L-glutamic acid in liquid phase (kmol/m^3)
$C_{\mathrm{A}^{2-}}$	equilibrium concentration of A^{2-} type of L-glutamic acid in liquid phase (kmol/m^3)
K_1	first dissociation constant of L-glutamic acid (kmol/m^3)
K_2	second dissociation constant of L-glutamic acid (kmol/m^3)
K_3	third dissociation constant of L-glutamic acid (kmol/m^3)
$K_{\mathrm{A}^\pm}$	equilibrium constant for adsorption of $\mathrm{A}^\pm$ type of L-glutamic acid on ChF-B (Eq. 20) (m^3/kmol)
K_{HCl}	equilibrium constant for adsorption of HCl on ChF-B (Eq. 3) (m^3/kmol)
m_i	association number in Langmuir–Freundlich equation
Q_{A}	saturation capacity of L-glutamic acid (mol/kg of dry fiber)
Q_{HCl}	concentration of primary amino group of chitosan fixed in ChF-B (mol/kg of dry fiber)
q_{A}	equilibrium concentration of L-glutamic acid in adsorbent phase (mol/kg of dry fiber)
q_{HCl}	equilibrium concentration of HCl adsorbed on ChF-B (mol/kg of dry fiber)
V	volume of solution (m^3)
W	weight of dry fiber (kg)
A^+	L-glutamic acid of $\mathrm{Ra{-}NH_3^+(-COOH)_2}$
$\mathrm{A}^\pm$	L-glutamic acid of $\mathrm{Ra{-}NH_3^+(-COO^-)(-COOH)}$
A^-	L-glutamic acid of $\mathrm{Ra{-}NH_3^+(-COO^-)_2}$
A^{2-}	L-glutamic acid of $\mathrm{Ra{-}NH_2(-COO^-)_2}$
$\mathrm{R{-}NH_2}$	primary ammonium group of ChF-B

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