# Adsorption of Glutamic Acid on Polyaminated Highly Porous Chitosan: Equilibria

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Adsorption of L-glutamic acid on the polyaminated highly porous chitosan (PEI-CH) appeared technically feasible. The saturation capacity for adsorption of L-glutamic acid was about 1.43 times larger than a commercial weakly basic ion exchanger DIAION WA30. The experimental equilibrium isotherm ($q_A$–$C_{TA}$ curve) for adsorption of L-glutamic acid on PEI-CH was independent of the initial concentration of L-glutamic acid but depended on pH of the solution significantly. It appeared that the adsorption of L-glutamic acid was controlled by the acid/base neutralization reaction between neutral L-glutamic acid (zwitterion, $A^{\pm}$) and the weakly basic ion exchanger. The significant effect of pH on the $q_A$–$C_{TA}$ curve disappeared in the $q_A$–$C_{A^{\pm}}$ curve. Theoretical equations for equilibrium isotherms for adsorption of L-glutamic acid on PEI-CH were derived by assuming neutralization reaction between the carboxylic group of the neutral L-glutamic acid and each three different fixed amino groups of PEI-CH. The theoretical equations correlated the experimental equilibrium isotherms well.

## 1. Introduction

In the food, health product, and medicine industries, ion exchange resins have been generally and extensively used for the separation, purification, and recovery of amino acids. In these applications, ion exchange resins are particularly effective since the net charge on these molecules may vary in magnitude and sign when the pH of the solution changes. An amino acid is adsorbed on an ion exchange resin at a certain solution at which the molecule has a charge opposite to that of the resin. The amino acid may be desorbed by changing the pH of the solution to a value such that its net charge is the same as that of the resin. Therefore it is important to study the representation of uptake equilibria of amino acids on ion exchange resins as a function of solution composition. Several investigations on equilibria for adsorption of amino acids on ion exchange resins have been reported. Seno and Yamabe (1960, 1961) reported the way in which the pH of the solution affects the uptake equilibria of amino acids. They presented experimental results for adsorption of some neutral, acidic, and basic amino acids on four different commercial ion exchangers: strongly and weakly acidic ion exchange resins and strongly and weakly basic ion exchange resins. They assumed that the amino acids were adsorbed on strongly acidic or basic ion exchange resins by ion exchange reaction and presented a theoretical equation for the equilibrium. They showed theoretically that the amount of the amino acid adsorbed was the largest at the isoelectric point of amino acid. They compared the theoretical equations for the equilibrium isotherms with the experimental value qualitatively, but not quantitatively. Hino et al. (1961) reported the experimental saturation capacity of various amino acids on several ion exchangers. Haynes (1967) 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. Saunders et al. (1989) studied the uptake of phenylalanine and tyrosine by the hydrogen form of macroreticular strongly acidic cation exchange resin and showed that the amino acids were adsorbed by the stoichiometric ion exchange. Gosling et al. (1989) studied experimentally the role of adsorption isotherms in the design of chromatographic separations for downstream processing for tryptophan and aspartic acid onto the anion exchanger. Dye et al. (1990) investigated the equilibria for adsorption of amino acids on a strong-acid cation exchange resin. They showed that the uptake of an amino acid by the hydrogen form of the resin occured primarily as the result of the stoichiometric exchange of amino acid cations for hydrogen ion. DeCarli (1990) reported the operation of a continuous displacement chromatograph for the separations of dilute mixtures of amino acids by displacement development using a cation exchange resin. Helfferich (1990) derived the 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. These above investigations are mainly adsorption of amino acids on strongly acidic or strongly basic ion exchangers. The equilibrium isotherms for adsorption of an amino acid on weakly basic or weakly acidic ion exchangers especially in the theoretical investigations have not been reported.

In our previous work (Yoshida et al., 1994), we reported that a new weakly basic ion exchanger, highly porous polyaminated chitosan (hereafter called PEI-CH), was technically feasible for removal and/or recovery of the strong acid from aqueous solutions. The saturation capacity for adsorption of HCl on PEI-CH was about 1.75 times larger than that of a commercial weakly basic resin DIAION WA30. PEI-CH has at least four different fixed groups, the primary ammonium group of chitosan and primary, secondary, and tertiary ammonium groups of PEI. Theoretical equations for the equilibrium isotherms were derived by assuming acid/base neutralization between strong acid and the four amino groups fixed in the resins.

In the present work, we investigate the possibility of using PEI-CH for adsorption of L-glutamic acid. The experimental equilibrium isotherm for adsorption of L-glutamic acid on PEI-CH is compared with that on DIAION WA30 for the case that there exist no electrolytes except for L-glutamic acid in the solution. The effect of pH on the equilibrium amount of L-glutamic acid adsorbed on PEI-CH and on DIAION WA30 (hereafter called $q_A$–pH curve) is also presented. Further

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**Table 1. Experimental Physical Properties of PEI-CH and DIAION WA30[a]**

| | PEI-CH | WA30 |
|---|---|---|
| concn of amino groups fixed in adsorbent phase, $Q$ (kmol/m$^3$ of wet resin) | 2.58 | 1.48 |
| water content (kg of water/kg of wet resin) | 0.632 | 0.541 |
| density | | |
| true (kg of dry resin/m$^3$ of wet resin) | 1360 | 1063 |
| apparent (kg of wet resin/m$^3$ of wet resin) | 1106 | 1026 |
| porosity | 0.700 | 0.557 |
| particle diameter (mm) | 0.313 | 0.421 |

[a] Yoshida et al. (1994).

the equilibrium isotherms at different constant values of pH are given. Theoretical equations for equilibrium isotherm and $q_A$–pH curve for adsorption of L-glutamic acid on PEI-CH are developed by assuming the neutralization reaction of L-glutamic acid with each functional group of PEI-CH. The way in which the equilibrium coefficients for adsorption of L-glutamic acids on each functional group are determined is shown. The theoretical equations are compared with the experimental equilibrium isotherms and the $q_A$–pH curve.

## 2. Materials

PEI-CH and DIAION WA30 (Mitsubishi Kasei Co.) have been used in this experimental study. They are the same as those used for the adsorption of HCl in our previous paper (Yoshida et al., 1994). The experimental physical properties of PEI-CH and DIAION WA30 are given in Table 1. PEI-CH has been developed by introducing poly(ethylene imine) (hereafter called PEI), with a molecular weight of 10 000 into the macropore of the cross-linked chitosan. The details of the fabrication method are given by Kawamura et al. (1993). DIAION WA30 is a commercial weakly basic ion exchanger. The network of WA30 is styrene–divinylbenzene, and its functional group is tertiary amine. The properties of both resins were explained in more detail in the previous paper (Yoshida et al., 1994).

## 3. Experimental Section

The resin particles which were free from adsorbates were prepared according to the same procedure as the previous paper (Yoshida et al., 1994). L-Glutamic acid was the guaranteed reagent (Tokyo Kasei Co.). The pH of the L-glutamic acid solution was adjusted using HCl or NaOH. The equilibrium isotherms for adsorption of L-glutamic acid were measured by the batch method. The equilibrium was fully reached in 4 days. In addition, 4 days were sufficiently enough to reach the equilibrium for both resins because of our breakthrough curve experiments. The solutions for L-glutamic acid was analyzed with a Shimadzu liquid chromatograph Model LC-3A and a Shimadzu fluorescence HPLC monitor Model RF-535. This system is based on the NaClO/OPA nonswitching method. The pH of the solution was determined using a Horiba pH meter Model F-16. The adsorbed phase concentration of L-glutamic acid was calculated according to

$$q_A = \frac{V(C_0 - C_{TA})}{W} \tag{1}$$

where $C_0$ and $C_{TA}$ are the initial concentration and equilibrium concentration of L-glutamic acid in the liquid phase (kmol/m$^3$), respectively. $q_A$ denotes equilibrium concentration of L-glutamic acid in the adsorbent phase (kmol/m$^3$ of wet resin). $V$ and $W$ are the volume of the solution and wet adsorbent particles (m$^3$), respectively. In the experimental study on the equilibrium, the values of $V/W$ were 55 – 2200.

All experiments were carried out at 298 K.

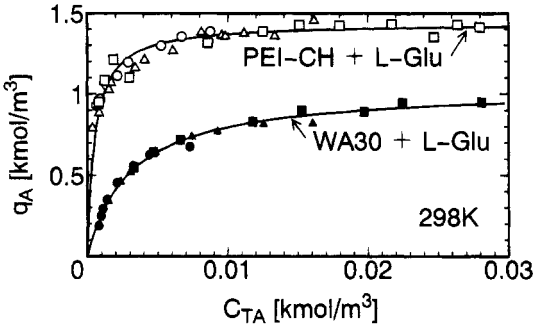



**Figure 1.** Equilibrium isotherms for adsorption of L-glutamic acid on PEI-CH and WA30 for the case that there existed no electrolyte except for L-glutamic acid in the solution. (○, ●) $C_0$ = 0.01 kmol/m$^3$, (△, ▲) $C_0$ = 0.02 kmol/m$^3$, (□, ■) $C_0$ = 0.03 kmol/m$^3$ (—) eq 2.

**Table 2. Experimental Langmuir Coefficients for the Case That There Existed No Electrolyte Except for L-Glutamic Acid in the Solution**

| | $K$ (m$^3$/kmol) | $Q_A$ (kmol/m$^3$) | $Q_A/Q$ |
|---|---|---|---|
| PEI-CH | $1.95 \times 10^3$ | 1.44 | 0.558 |
| WA30 | $3.27 \times 10^2$ | 1.04 | 0.703 |

## 4. Results

Figure 1 shows the experimental equilibrium isotherms for adsorption of L-glutamic acid on PEI-CH and DIAION WA30 for the case that there existed no electrolyte except for L-glutamic acid in the solution. The isotherms were measured for three different initial concentrations of L-glutamic acid ($C_0$). Since the experimental equilibrium isotherms are independent of $C_0$, L-glutamic acid may be adsorbed by chemisorption and the equilibrium isotherm may be expressed by the Langmuir equation:

$$q_A = \frac{KQ_AC_{TA}}{1 + KC_{TA}} \tag{2}$$

where $Q_A$ is the saturation capacity of L-glutamic acid (kmol/m$^3$ of wet resin) and $K$ shows the equilibrium constant (m$^3$/kmol). The solid lines in the figure show the Langmuir isotherm. The data are correlated well by eq 2. The Langmuir coefficients $K$ and $Q_A$ are listed in Table 2. They were determined using the following equation to which eq 2 was transformed.

$$C_{TA} = -\frac{1}{K} + Q_A\left(\frac{C_{TA}}{q_A}\right) \tag{3}$$

The data were plotted based on eq 3, that is, $C_{TA}$ vs $C_{TA}/q_A$ for PEI-CH and WA30. The data measured for three different $C_0$ were correlated well by the straight line without scattering. The values of $K$ and $Q_A$ were determined from the intercept and slope of the straight line, respectively. The saturation capacity for adsorption of L-glutamic acid on PEI-CH is about 1.43 times larger than that for WA30 (see Table 2). This result suggests that PEI-CH is more feasible for adsorption of L-glutamic acid than WA30. The saturation capacity $Q_A$ is smaller than the total concentration of fixed amino

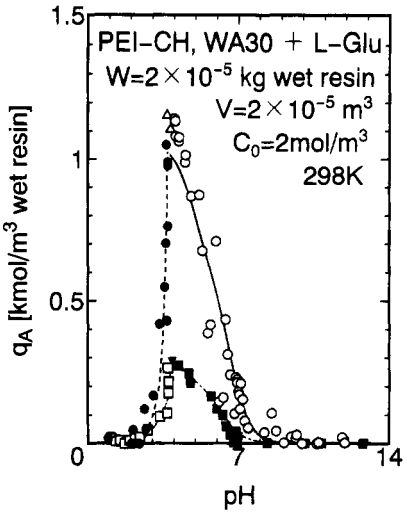



**Figure 2.** Effect of pH on the equilibrium amount of L-glutamic acid adsorbed on PEI-CH and WA30. (●) With HCl system (PEI-CH), (○) with NaOH system (PEI-CH), (△) without inorganic electrolyte (PEI-CH), (□) with HCl system (WA30), (■) with NaOH system (WA30), (▼) without inorganic electrolyte (WA30). (- - -) Theoretical line calculated from eqs 41, 44, and 46. (—) Theoretical line calculated from eqs 28 and 44.

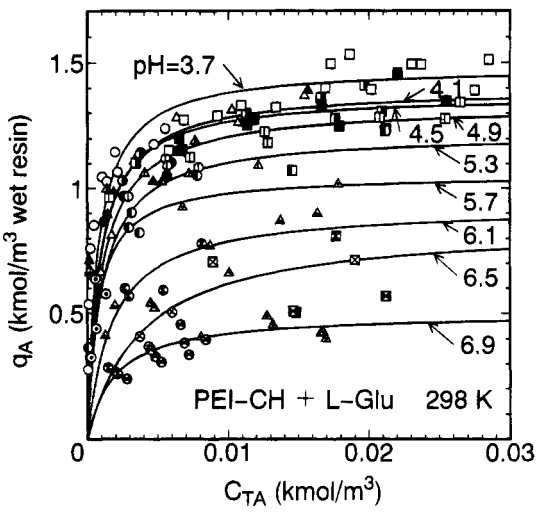



**Figure 3.** Equilibrium isotherms for adsorption of L-glutamic acid on PEI-CH at constant pH which was adjusted using NaOH. (—) Equation 2.

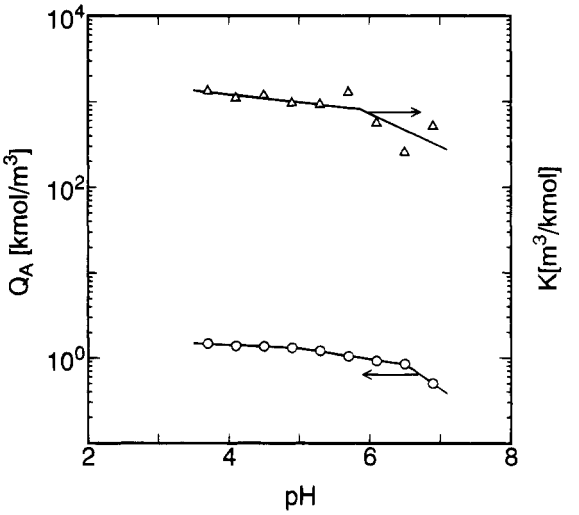



**Figure 4.** Effect of pH on saturation capacity $Q_A$ and equilibrium constant $K$. (—) Equation 4.

groups of the resin $Q$ as shown in Table 2. This will be discussed in the theoretical section in detail.

Figure 2 shows the effect of pH on the equilibrium amount of L-glutamic acid adsorbed on PEI-CH and WA30. The data were obtained by the batch method. The volume of the solution $V$ was $2 \times 10^{-5}$ m$^3$, the weight of the resin $W'$ was $2 \times 10^{-5}$ kg of wet resin, and the initial concentration of L-glutamic acid $C_0$ was $2 \times 10^{-3}$ kmol/m$^3$ for each datum. The initial value of the pH of each solution was adjusted using HCl or NaOH (see the keys in Figure 2). The pH value of each datum in the figure was the final equilibrium value. The experimental $q_A$–pH curve for PEI-CH is similar to that for WA30. Only when $2 < pH < 10$, L-glutamic acid is adsorbed on the resins. Both $q_A$–pH curves show a peak when the pH of the solution is about the isoelectric point of L-glutamic acid ($pI = 3.22$ (Yamakawa et al., 1979)). However, the peak of the curve for PEI-CH is about 4 times larger than that for WA30. Since from the results of Figures 1 and 2, PEI-CH may be more feasible as the adsorbent of L-glutamic acid than WA30, we investigated the equilibrium isotherm for adsorption of L-glutamic acid on PEI-CH in more detail.

As the $q_A$–pH curve of PEI-CH is sharp, the separation process that L-glutamic acid is adsorbed on it at $pH \cong pI$ and is desorbed at $pH < 2$ or $pH > 10$ may be technically feasible. In order to make clear the effect of the pH on the adsorption of L-glutamic acid, we measured the equilibrium isotherms at different constant pH values (±0.2) and the results for PEI-CH are given in Figure 3. The pH values were adjusted by using NaOH. 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 the resin is largest at pH 3.7 and it decreases with increasing pH. In addition, since the $q_A$–pH curve for $pH < 3.7$ is very sharp as shown in Figure 2, it was impossible to maintain pH constant and we could not obtain the equilibrium isotherms for constant pH in $pH < 3.7$. The solid lines in Figure 3 show the Langmuir isotherms (eq 2). The correlation coefficients at pH = 3.7, 4.1, 4.5, 4.9, 5.3, 5.7, 6.1, 6.5, and 6.9 are 0.997, 0.997, 0.995, 0.998, 0.996, 0.999, 0.991, 0.983, and 0.956, respectively. The saturation capacity $Q_A$ and equilibrium constant $K$ were determined according to the plots based on eq 3 as mentioned earlier. Figure 4 shows that $Q_A$ and $K$ for PEI-CH decrease with increasing pH especially in $pH > 6$. The data give the following estimating equations for $Q_A$ and $K$.

PEI-CH

$$\log Q_A = -3.7 \times 10^{-2}pH + 3.0 \times 10^{-1} \quad (3.5 < pH < 5.0)$$

$$\log Q_A = -1.3 \times 10^{-1}pH + 7.4 \times 10^{-1} \quad (5.0 < pH < 6.5)$$

$$\log Q_A = -5.8 \times 10^{-1}pH + 3.7 \quad (6.5 < pH < 7.1)$$

$$\log K = -9.3 \times 10^{-2}pH + 3.5 \quad (3.5 < pH < 5.9)$$

$$\log K = -3.8 \times 10^{-1}pH + 5.2 \quad (5.9 < pH < 7.1) \quad (4)$$

## 5. Equilibrium Theory (PEI-CH)

The following conclusions were obtained from the above experimental study: (i) When only L-glutamic acid dissolved in water, the equilibrium isotherm was correlated by the Langmuir equation. The saturation

capacity was about 56% and 70% of the total concentration of the fixed amino groups of PEI-CH and WA30, respectively (Table 2). (ii) The $q_A$–pH curve showed that L-glutamic acid was adsorbed only the region in 2 < pH < 10 and the peak appeared around pH = p$I$. (iii) When the pH was constant, the isotherm was independent of the initial concentration of L-glutamic acid but depended on the pH significantly. The isotherm for each constant pH value was correlated by the Langmuir equation.

In order to understand the above complicated results and to estimate equilibrium isotherms in any conditions, a theoretical analysis is necessary. Any theoretical investigations on equilibrium isotherm for adsorption of an amino acid on weakly basic or weakly acidic ion exchangers have not been reported, although Seno and Yamabe (1960, 1961), Helfferich (1990), and Dye et al. (1990) have reported the theoretical works for adsorption of amino acids on strongly acid ion exchangers.

PEI-CH is essentially weakly basic ion exchanger, because four different functional groups in the resin are weakly basic. Since those functional groups do not have $OH^-$ in the acid region especially when pH < 5, the maximum of the uptake in Figure 2 may not be explained by the ion exchange between $OH^-$ and negatively charged glutamic acid.

L-Glutamic acid dissociates as follows:

$$Ra{-}NH_3^+(-COOH)_2 \overset{K_1}{\rightleftharpoons} Ra{-}NH_3^+(-COO^-)(-COOH) + H^+ \quad (5)$$

$$Ra{-}NH_3^+(-COO^-)(-COOH) \overset{K_2}{\rightleftharpoons} Ra{-}NH_3^+(-COO^-)_2 + H^+ \quad (6)$$

$$Ra{-}NH_3^+(-COO^-)_2 \overset{K_3}{\rightleftharpoons} Ra{-}NH_2(-COO^-)_2 + H^+ \quad (7)$$

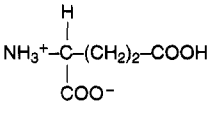
The equilibrium relations for eqs 5–7 are given by eqs 8–10, respectively.

$$K_1 = \frac{C_{A^\pm} C_{H^+}}{C_{A^+}} \quad (8)$$

$$K_2 = \frac{C_{A^-} C_{H^+}}{C_{A^\pm}} \quad (9)$$

$$K_3 = \frac{C_{A^{2-}} C_{H^+}}{C_{A^-}} \quad (10)$$

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




is expressed by $Ra{-}NH_3^+(-COO^-)(-COOH)$. Figure 5 shows their theoretical concentration distributions in the liquid phase calculated from eqs 8–10 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$^3$ (Yamakawa et al., 1979). The distribution curve of $A^\pm$ is similar to the experimental $q_A$–pH curve in Figure 2. This may suggest that L-glutamic acid is adsorbed on a weakly basic resin

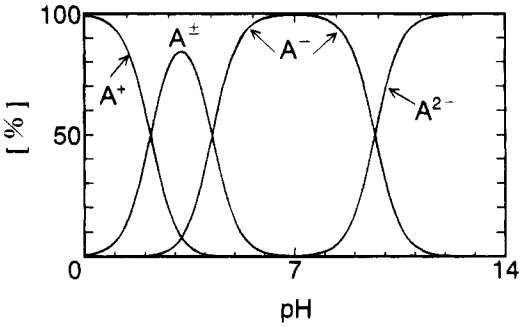



**Figure 5.** Theoretical concentration distributions of L-glutamic acid in the liquid phase.

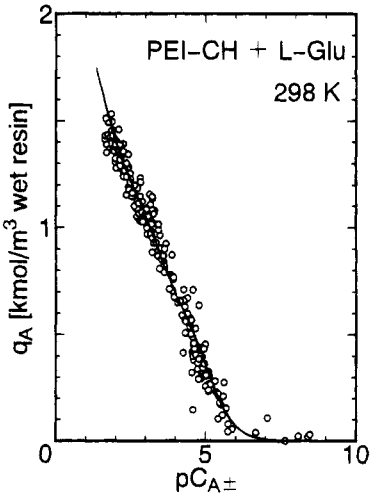



**Figure 6.** Relation between $q_A$ and $pC_{A^\pm}$ (=−log $C_{A^\pm}$) for PEI-CH without HCl system. (—) Equation 28.

according to the following, an acid/base neutralization reaction:

$$R{-}N + \begin{matrix} COO^- \\ | \\ Ra{-}NH_3^+ \\ | \\ COOH \end{matrix} \rightleftharpoons R{-}NH^+ \left( \begin{matrix} COO^- \\ | \\ Ra{-}NH_3^+ \\ | \\ COO^- \end{matrix} \right) \quad (11)$$

Equation 11 is simply written by

$$R{-}N + A^\pm \rightleftharpoons R{-}NH^+A^- \quad (12)$$

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

$$C_{A^\pm} = \frac{C_{TA}}{1 + \frac{C_{H^+}}{K_1} + \frac{K_2}{C_{H^+}} + \frac{K_2 K_3}{C_{H^+}^2}} \quad (13)$$

$$C_{TA} = C_{A^+} + C_{A^\pm} + C_{A^-} + C_{A^{2-}} \quad (14)$$

Equation 11 or 12 implies that the equilibrium isotherm for adsorption of L-glutamic acid on a weakly basic resin is given by an equation in which $q_A$ is expressed by only one independent variable $C_{A^\pm}$.

**5.1. Without HCl System.** Figure 6 shows the relation between $q_A$ and $pC_{A^\pm}$ (=−log $C_{A^\pm}$) for PEI-CH using the data for the without HCl system (all data in Figure 1, the data without HCl shown by open keys in Figure 2, and all data in Figure 3). This figure proves the above discussion. The significant effect of pH on the $q_A$–$C_{TA}$ curve in Figure 3 disappears in the $q_A$–$pC_{A^\pm}$

**Table 3. Experimental Equilibrium Coefficients for PEI-CH**

| | *i* | | | | |
|---|---|---|---|---|---|
| | C | P1 | P2 | P3 | total |
| $Q_i$ (kmol/m$^3$) | 0.632[a] | 0.539[a] | 0.908[a] | 0.576[a] | 2.66[a] |
| $K_{i,HCl}$ (m$^3$/kmol) | $2.00 \times 10^{6}$[a] | $2.89 \times 10^{2}$[a] | $1.93 \times 10^{3}$[a] | $3.68 \times 10^{4}$[a] | |
| $K_{i,A}$ (m$^3$/kmol) | $1.23 \times 10^{5}$ | – | 30 | $2.28 \times 10^{3}$ | |

[a] Yoshida et al. (1994).

curve in Figure 6. This is because in Figure 6 the effect of pH is considered in the calculation of $C_{A^\pm}$ from eqs 13 and 14. In addition, we also plotted $q_A$ vs $pC_{A^+}$, $pC_{A^-}$, and $pC_{A^{2-}}$ using the same data as the ones in Figure 6, respectively, but the plots were very scattered. These results suggest that the reaction mechanism eq 11, which is proposed here, may be acceptable.

It was proved that PEI-CH has four different fixed amino groups, primary ammonium group of chitosan and primary, secondary, and tertiary ammonium groups of PEI fixed in PEI-CH (Yoshida et al., 1994). They are denoted as $R_C-NH_2$, $R_{P1}-NH_2$, $R_{P2}-NH$, and $R_{P3}-N$, respectively. Their concentrations in the adsorbent phase (kmol/m$^3$), $Q_C$, $Q_{P1}$, $Q_{P2}$, and $Q_{P3}$, were determined from the experimental titration curve of HCl as shown in Table 3 (Yoshida et al., 1994). From the above discussion on Figure 6, it can be assumed that the $A^\pm$ type of L-glutamic acid is adsorbed on each functional group of PEI-CH by an acid/base neutralization reaction, and eq 12 is rewritten as follows:

$$R_C-NH_2 + A^\pm \overset{K_{C,A}}{\rightleftharpoons} R_C-NH_3^+A^- \quad (15)$$

$$R_{P3}-N + A^\pm \overset{K_{P3,A}}{\rightleftharpoons} R_{P3}-NH^+A^- \quad (16)$$

$$R_{P2}-NH + A^\pm \overset{K_{P2,A}}{\rightleftharpoons} R_{P2}-NH_2^+A^- \quad (17)$$

$$R_{P1}-NH_2 + A^\pm \overset{K_{P1,A}}{\rightleftharpoons} R_{P1}-NH_3^+A^- \quad (18)$$

Applying the mass action law to eqs 15–18, the equilibrium relation for each functional group is given as follows:

$$q_{C,A} = \frac{K_{C,A}Q_C C_{A^\pm}}{1 + K_{C,A}C_{A^\pm}} \quad (19)$$

$$q_{P3,A} = \frac{K_{P3,A}Q_{P3}C_{A^\pm}}{1 + K_{P3,A}C_{A^\pm}} \quad (20)$$

$$q_{P2,A} = \frac{K_{P2,A}Q_{P2}C_{A^\pm}}{1 + K_{P2,A}C_{A^\pm}} \quad (21)$$

$$q_{P1,A} = \frac{K_{P1,A}Q_{P1}C_{A^\pm}}{1 + K_{P1,A}C_{A^\pm}} \quad (22)$$

where $q_{C,A}$, $q_{P3,A}$, $q_{P2,A}$, and $q_{P1,A}$ denote the equilibrium amount of L-glutamic acid adsorbed on $R_C-NH_2$, $R_{P3}-N$, $R_{P2}-NH$ and $R_{P1}-NH_2$, respectively (kmol/m$^3$). Assuming the reactions of eqs 15–18 occur simultaneously, the total amount of L-glutamic acid adsorbed on PEI-CH is given by

$$q_A = q_{C,A} + q_{P3,A} + q_{P2,A} + q_{P1,A} = \frac{K_{C,A}Q_C C_{A^\pm}}{1 + K_{C,A}C_{A^\pm}} + \frac{K_{P3,A}Q_{P3}C_{A^\pm}}{1 + K_{P3,A}C_{A^\pm}} + \frac{K_{P2,A}Q_{P2}C_{A^\pm}}{1 + K_{P2,A}C_{A^\pm}} + \frac{K_{P1,A}Q_{P1}C_{A^\pm}}{1 + K_{P1,A}C_{A^\pm}} \quad (23)$$

The order of basic strength of the functional groups is $R_C-NH_2 > R_{P3}-N > R_{P2}-NH > R_{P1}-NH_2$ (Yoshida et al., 1994). Since the values of $Q_C$, $Q_{P3}$, $Q_{P2}$, and $Q_{P1}$ had been determined (Table 3), equilibrium constants $K_{C,A}$, $K_{P3,A}$, $K_{P2,A}$, and $K_{P1,A}$ in eqs 19–23 are unknown and they are determined in turn as follows. We may assume that $A^\pm$ of L-glutamic acid is adsorbed mainly on $R_C-NH_2$, which shows the strongest basicity in the four fixed amino groups, when $pC_{A^\pm}$ is larger than about 5.1 (the first inflection point of Figure 6). Under this assumption, only eq 15 occurs in the $pC_{A^\pm}$ region and the isotherm is expressed by eq 24.

$$q_A = q_{C,A} = \frac{K_{C,A}Q_C C_{A^\pm}}{1 + K_{C,A}C_{A^\pm}} \quad (24)$$

Equation 24 is transformed to eq 25.

$$C_{A^\pm} = Q_C\frac{C_{A^\pm}}{q_A} - \frac{1}{K_{C,A}} \quad (25)$$

Figure 7 shows the plots of the data for $pC_{A^\pm} > 3.77$ based on eq 25. The data are correlated by the straight line when $pC_{A^\pm}$ is larger than about 4.3 ($C_{A^\pm}/q_A$ is smaller than about $7 \times 10^{-4}$). The slope of the straight line was determined using the value of $Q_C$ (Table 3). The intercept of the straight line was determined by the least squares method using the data for $pC_{A^\pm} > 4.3$. The correlation coefficient for all data for $pC_{A^\pm} > 4.3$ was 0.988. The value of $K_C$ obtained from the intercept is given in Table 3. When $pC_{A^\pm}$ is smaller than 4.3, the data deviate from the straight line, because the reactions of eqs 16–18 were neglected.

Next, it is assumed that $A^\pm$ of L-glutamic acid is adsorbed on $R_C-NH_2$, which shows the strongest basicity, and $R_{P3}-N$, which shows the second strongest basicity, simultaneously in the second $pC_{A^\pm}$ region in Figure 6. Under this assumption, eqs 15 and 16 occur simultaneously and the isotherm is given by eq 26. Equation 27 is obtained from eqs 19 and 26. In eqs 26

$$q_A = \frac{K_{C,A}Q_C C_{A^\pm}}{1 + K_{C,A}C_{A^\pm}} + \frac{K_{P3,A}Q_{P3}C_{A^\pm}}{1 + K_{P3,A}C_{A^\pm}} = q_{C,A} + \frac{K_{P3,A}Q_{P3}C_{A^\pm}}{1 + K_{P3,A}C_{A^\pm}} \quad (26)$$

$$C_{A^\pm} = Q_{P3}\frac{C_{A^\pm}}{q_A - q_{C,A}} - \frac{1}{K_{P3,A}} \quad (27)$$

and 27, $K_{C,A}$, $Q_C$, and $Q_{P3}$ are known parameters (Table 3). $q_{C,A}$ in eq 27 can be calculated for any value of $C_{A^\pm}$

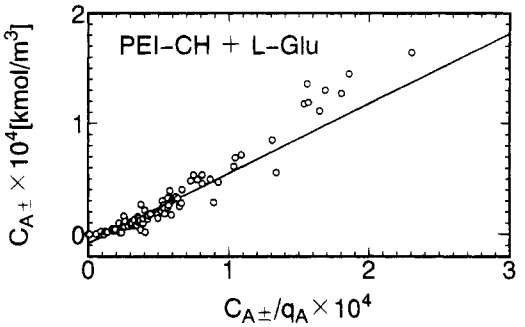



**Figure 7.** Plots of data for $pC_{A\pm} > 3.77$ for adsorption of L-glutamic acid on PEI-CH based on eq 25.

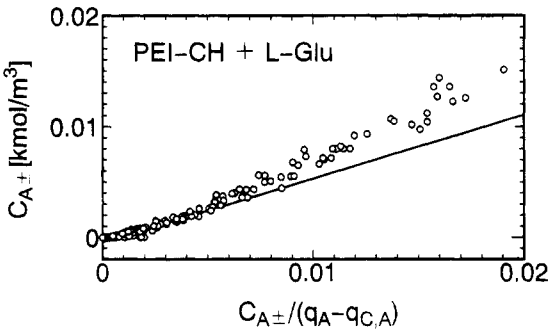



**Figure 8.** Plots of data for $1.82 < pC_{A\pm} < 4.3$ for adsorption of L-glutamic acid on PEI-CH based on eq 27.

using the known $K_{C,A}$ and $Q_C$ and eq 19. $K_{P3,A}$ is only unknown parameter. Figure 8 shows the plot of the data for $1.82 < pC_{A\pm} < 4.3$ based on eq 27. When $pC_{A\pm}$ is larger than about 2.6 ($C_{A\pm}/(q_A - q_{C,A})$ is smaller than about $5 \times 10^{-3}$), the data are correlated by the straight line. The slope of the straight line was determined using the value of $Q_{P3}$ (Table 3). The intercept of the straight line was determined by the least squares method using the data for $pC_{A\pm} > 2.6$. The correlation coefficient was 0.955. $K_{P3,A}$ obtained from the intercept is given in Table 3. When $pC_{A\pm}$ is smaller than 2.6, the data deviate from the straight line. This is caused by neglecting the reactions of eqs 17 and 18.

Similarly, assuming that eqs 15–17 occur simultaneously in the next $pC_{A\pm}$ region in the $q-pC_{A\pm}$ curve, eqs 28 and 29 are obtained:

$$q_A = \frac{K_{C,A}Q_C C_{A\pm}}{1+K_{C,A}C_{A\pm}} + \frac{K_{P3,A}Q_{P3}C_{A\pm}}{1+K_{P3,A}C_{A\pm}} + \frac{K_{P2,A}Q_{P2}C_{A\pm}}{1+K_{P2,A}C_{A\pm}} = q_{C,A} + q_{P3,A} + \frac{K_{P2,A}Q_{P2}C_{A\pm}}{1+K_{P2,A}C_{A\pm}} \quad (28)$$

$$C_{A\pm} = Q_{P2}\frac{C_{A\pm}}{q_A - (q_{C,A} + q_{P3,A})} - \frac{1}{K_{P2,A}} \quad (29)$$

where the coefficients, $K_{C,A}$, $Q_C$, $K_{P3,A}$, $Q_{P3}$, and $Q_{P2}$ are known parameters (see Table 3). $q_{C,A}$ and $q_{P3,A}$ in eq 29 can be calculated for any value of $C_{A\pm}$ using the known $K_{C,A}$ and $Q_C$ for eq 19, and $K_{P3,A}$ and $Q_{P3}$ for eq 20, respectively. $K_{P2,A}$ is the only unknown parameter. The data for $1.63 < pC_{A\pm} < 4.3$ were plotted based on eq 29, but the plots scattered significantly (correlation coefficient was 0.495) and $K_{P2,A}$ could not be determined from the above plot. This may be because the errors in the first and second coefficients propagated into errors in the third coefficient. Therefore, the value of $K_{P2,A}$ was determined by matching the experimental data in Figure 6 with eq 28. The solid line in Figure 6 was

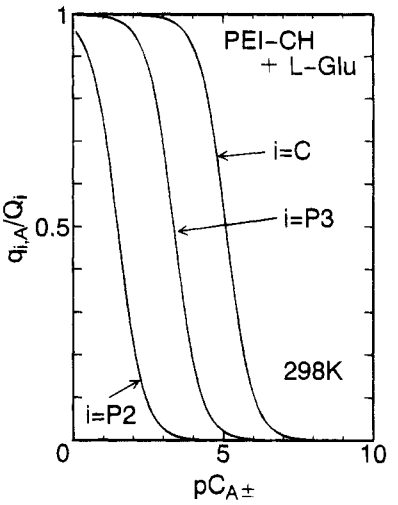



**Figure 9.** Relation between $q_{i,A}/Q_i$ and $pC_{A\pm}$ for adsorption of L-glutamic acid on PEI-CH. (—) Equations 19–21.

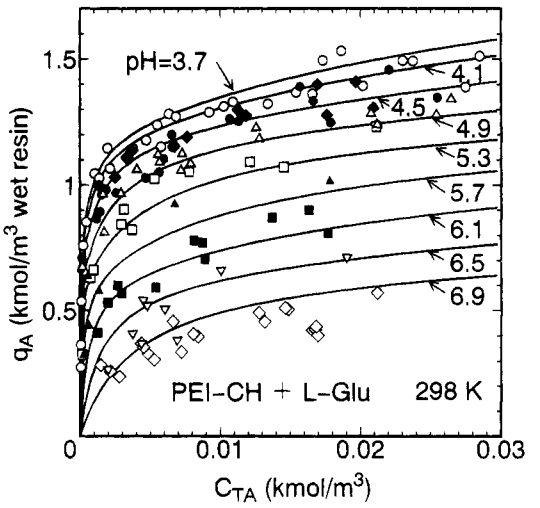



**Figure 10.** Equilibrium isotherms for adsorption of L-glutamic acid on PEI-CH at constant pH which was adjusted using NaOH. (—) Equations 13 and 28.

calculated from eq 28 using the equilibrium coefficients listed in Table 3. The data are correlated reasonably well by the solid line. The theoretical line does not exist in $pC_{A\pm} < 1.24$ because of the solubility of L-glutamic acid in water at 298 K. The solubility is $5.7 \times 10^{-2}$ kmol/m$^3$ (Yamakawa et al., 1979), which corresponds to $pC_{A\pm} = 1.24$. As mentioned earlier, the amount of L-glutamic acid on PEI-CH is the largest at pH = 3.7. The saturation capacity of L-glutamic acid on PEI-CH at pH = 3.7 was 1.48 kmol/m$^3$. The saturation capacity of L-glutamic acid without inorganic electrolyte system was 1.44 kmol/m$^3$ (Table 2). These saturation capacities are smaller than $Q_C + Q_{P3} + Q_{P2} = 2.12$ kmol/m$^3$. Therefore the reaction of eq 18 does not have to be considered in the theoretical analysis, and eq 28 is sufficient to get the theoretical equilibrium isotherm. Figure 9 shows the theoretical relation between $q_{i,A}/Q_i$ and $pC_{A\pm}$ for adsorption of L-glutamic acid on PEI-CH. $q_{i,A}/Q_i$ was calculated from eqs 19, 20, and 21 for $i$ = C, P3, and P2, respectively. When $pC_{A\pm} = 1.24$, $q_{C,A}/Q_C \cong 1$, $q_{P3,A}/Q_{P3} \cong 0.98$, and $q_{P2,A}/Q_{P2} \cong 0.35$. As mentioned above, $pC_{A\pm} > 1.24$. In $pC_{A\pm} > 1.24$, $R_C-NH_2$ and $R_{P3}-N$ mainly contribute to adsorption of L-glutamic acid and the contribution of $R_{P2}-NH$ is small. Therefore, the adsorption of L-glutamic acid on $R_{P1}-NH_2$ may be

negligible and eq 28 is sufficient to get the theoretical equilibrium isotherm.

Figure 10 shows the same experimental equilibrium isotherms as Figure 3. The solid lines represent the theoretical lines calculated from eqs 13 and 28 using the equilibrium coefficients $Q_i$ and $K_{i,A}$ given in Table 3. The experimental isotherm is correlated well by the solid line for each constant pH.

**5.2. With HCl System.** When HCl exists in aqueous solution of L-glutamic acid, L-glutamic acid and HCl are adsorbed on each functional group of PEI-CH by an acid/base neutralization reaction simultaneously. The reactions for adsorption of L-glutamic acid on each fixed ammonium group of PEI-CH, $R_C-NH_2$, $R_{P3}-N$, and $R_{P2}-NH$ are expressed by eqs 15–17. The adsorption of L-glutamic acid on $R_{P1}-NH_2$ given by eq 18 may be neglected by the reason mentioned in the above section. The reactions for adsorption of HCl on PEI-CH are shown as follows:

$$R_C-NH_2 + HCl \overset{K_{C,HCl}}{\rightleftharpoons} R_C-NH_3^+Cl^- \quad (30)$$

$$R_{P3}-N + HCl \overset{K_{P3,HCl}}{\rightleftharpoons} R_{P3}-NH^+Cl^- \quad (31)$$

$$R_{P2}-NH + HCl \overset{K_{P2,HCl}}{\rightleftharpoons} R_{P2}-NH_2^+Cl^- \quad (32)$$

$$R_{P1}-NH_2 + HCl \overset{K_{P1,HCl}}{\rightleftharpoons} R_{P1}-NH_3^+Cl^- \quad (33)$$

Applying the mass action law to eqs 15–17 and eqs 30–33, equilibrium solid phase concentrations of L-glutamic acid and HCl are given by

$$q_{C,A} = \frac{K_{C,A}Q_C C_{A^\pm}}{1 + K_{C,A}C_{A^\pm} + K_{C,HCl}C_{HCl}} \quad (34)$$

$$q_{P3,A} = \frac{K_{P3,A}Q_{P3} C_{A^\pm}}{1 + K_{P3,A}C_{A^\pm} + K_{P3,HCl}C_{HCl}} \quad (35)$$

$$q_{P2,A} = \frac{K_{P2,A}Q_{P2} C_{A^\pm}}{1 + K_{P2,A}C_{A^\pm} + K_{P2,HCl}C_{HCl}} \quad (36)$$

$$q_{C,HCl} = \frac{K_{C,HCl}Q_C C_{HCl}}{1 + K_{C,A}C_{A^\pm} + K_{C,HCl}C_{HCl}} \quad (37)$$

$$q_{P3,HCl} = \frac{K_{P3,HCl}Q_{P3} C_{HCl}}{1 + K_{P3,A}C_{A^\pm} + K_{P3,HCl}C_{HCl}} \quad (38)$$

$$q_{P2,HCl} = \frac{K_{P2,HCl}Q_{P2} C_{HCl}}{1 + K_{P2,A}C_{A^\pm} + K_{P2,HCl}C_{HCl}} \quad (39)$$

$$q_{P1,HCl} = \frac{K_{P1,HCl}Q_{P1} C_{HCl}}{1 + K_{P1,HCl}C_{HCl}} \quad (40)$$

where $C_{HCl}$ is the equilibrium concentration of HCl in the liquid phase (kmol/m$^3$). $K_{C,HCl}$, $K_{P3,HCl}$, $K_{P2,HCl}$, and $K_{P1,HCl}$ denote the equilibrium constants for adsorption of HCl on $R_C-NH_2$, $R_{P3}-N$, $R_{P2}-NH$, and $R_{P1}-NH_2$, respectively (m$^3$/kmol). The experimental values of $K_{i,HCl}$, which were presented in our previous paper (Yoshida et al., 1994), are given in Table 3. The total amount of L-glutamic acid adsorbed on PEI-CH is given by eq 41, which is a theoretical equilibrium isotherm

$$q_A = q_{C,A} + q_{P3,A} + q_{P2,A}$$
$$= \frac{K_{C,A}Q_C C_{A^\pm}}{1 + K_{C,A}C_{A^\pm} + K_{C,HCl}C_{HCl}} + \frac{K_{P3,A}Q_{P3} C_{A^\pm}}{1 + K_{P3,A}C_{A^\pm} + K_{P3,HCl}C_{HCl}} + \frac{K_{P2,A}Q_{P2} C_{A^\pm}}{1 + K_{P2,A}C_{A^\pm} + K_{P2,HCl}C_{HCl}} \quad (41)$$

with HCl system. In addition, the total amount of HCl in the adsorbent phase is given by eq 42. As all

$$q_{HCl} = q_{C,HCl} + q_{P3,HCl} + q_{P2,HCl} + q_{P1,HCl}$$
$$= \frac{K_{C,HCl}Q_C C_{HCl}}{1 + K_{C,A}C_{A^\pm} + K_{C,HCl}C_{HCl}} + \frac{K_{P3,HCl}Q_{P3} C_{HCl}}{1 + K_{P3,A}C_{A^\pm} + K_{P3,HCl}C_{HCl}} + \frac{K_{P2,HCl}Q_{P2} C_{HCl}}{1 + K_{P2,A}C_{A^\pm} + K_{P2,HCl}C_{HCl}} + \frac{K_{P1,HCl}Q_{P1} C_{HCl}}{1 + K_{P1,HCl}C_{HCl}} \quad (42)$$

equilibrium coefficients $K_{i,A}$, $K_{i,HCl}$, and $Q_i$ are known now, theoretical equilibrium isotherms can be calculated from eq 41, when HCl exists in the solution. Equation 41 should be tested by comparing experimental equilibrium isotherms for constant pH. However, the experimental isotherms at constant pH for adsorption of L-glutamic acid with HCl could not be obtained, because it was difficult to maintain pH of the solution constant. Therefore, the theoretical $q_A$–pH curve was calculated using eq 41 and it was compared with the experimental $q_A$–pH curve with HCl system (Figure 2). Equation 28 was also tested by comparing with the experimental $q_A$–pH curve without HCl system (Figure 2).

**5.3. Theoretical $q_A$–pH Curve.** Theoretical $q_A$–pH curves with HCl system and without HCl system were calculated using eqs 28 and 41, respectively.

The experimental adsorbed phase concentrations of L-glutamic acid given in Figure 2 were calculated according to eq 1. Equation 1 is transformed to eq 43.

$$C_{TA} = C_0 - q_A\frac{W}{V} \quad (43)$$

Substituting eq 43 into eq 13, eq 44 is obtained. When

$$C_{A^\pm} = \frac{C_0 - q_A\frac{W}{V}}{1 + \frac{C_{H^+}}{K_1} + \frac{K_2}{C_{H^+}} + \frac{K_2K_3}{C_{H^+}^2}} \quad (44)$$

HCl exists in the solution, the concentration of HCl is necessary because of eq 41. The condition of electroneutrality is given by eq 45. When $C_{Cl^-} < C_{H^+}$, $C_{HCl}$ is

$$C_{H^+} + C_{A^+} = C_{A^-} + 2C_{A^{2-}} + C_{OH^-} + C_{Cl^-} \quad (45)$$

calculated from eq 46, which is derived from eqs 8–10 and 45. When $C_{Cl^-} > C_{H^+}$, $C_{HCl}$ is equal to $C_{H^+}$.

$$C_{HCl} = C_{Cl^-} = C_{H^+} - \frac{K_W}{C_{H^+}} + \left(\frac{C_{H^+}}{K_1} - \frac{K_2}{C_{H^+}} - \frac{2K_2K_3}{C_{H^+}^2}\right)C_{A^\pm} \quad (46)$$

The dashed line in Figure 2 was the theoretical line (with HCl) calculated from eqs 41, 44, and 46. Equilibrium coefficients $Q_i$, $K_{i,A}$, and $K_{i,HCl}$ in eq 41 are given in Table 3. $C_0$, $W$, and $V$ in eq 44 were $2 \times 10^{-3}$ kmol/m$^3$, $2 \times 10^{-5}$ kg, and $2 \times 10^{-5}$ m$^3$, respectively. Dissociation constants of L-glutamic acid, $K_1$, $K_2$, and $K_3$ were $6.46 \times 10^{-3}$, $5.62 \times 10^{-5}$, and $2.14 \times 10^{-10}$ kmol/m$^3$, respectively (Yamakawa et al., 1979). The value of $q_A$ was assumed for a given value of $C_{H^+}$. The value of $C_{A^\pm}$ was calculated from eq 44 using the $C_{H^+}$ value and the assumed $q_A$. Thereafter, the value of $C_{HCl}$ was calculated from eq 46 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 41, 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 41, 44, and 46. 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 became within $10^{-6}$. The dashed line agrees reasonably well with the experimental $q_A$–pH curve with HCl system in pH < 3.7.

When the pH of the solution is adjusted using NaOH or no inorganic electrolytes exist in the solution, only L-glutamic acid is adsorbed on PEI-CH. The solid line in Figure 2 was a theoretical line (without HCl system) calculated from eqs 28 and 44. Equilibrium coefficients $Q_i$ and $K_{i,A}$ in eq 28 are given in Table 3. The value of $q_A$ was assumed for a given value of $C_{H^+}$. The value of $C_{A^\pm}$ was calculated from eq 44 using the $C_{H^+}$ value and the assumed $q_A$. Substituting the value of $C_{A^\pm}$ into eq 28, 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 28 and 44. 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 became within $10^{-6}$. The solid line agrees reasonably well with the experimental $q_A$–pH curve without HCl system in pH > 3.7.

## 6. Conclusion

The adsorption of L-glutamic acid on the polyaminated highly porous chitosan (PEI-CH) appeared technically feasible.

1. The saturation capacity for adsorption of L-glutamic acid was about 1.43 times larger than that for a commercial weakly basic ion exchanger DIAION WA30.

2. The experimental equilibrium isotherm ($q_A$–$C_{TA}$ curve) for adsorption of L-glutamic acid on PEI-CH was independent of the initial concentration of L-glutamic acid but depended significantly on the pH of the solution.

3. It appeared that L-glutamic acid was not adsorbed by stoichiometric ion exchange but by the acid/base neutralization reaction between $A^\pm$ type of L-glutamic acid and the weakly basic functional groups in the ion exchanger. The significant effect of pH on the $q_A$–$C_{TA}$ curve disappeared in the $q_A$–$C_{A^\pm}$ curve.

4. Theoretical equations for the equilibrium isotherm and $q_A$–pH curve were derived by assuming that the $A^\pm$ type of L-glutamic acid was adsorbed by the acid/base neutralization reaction on three different fixed amino groups on PEI-CH, $R_C$–$NH_2$, $R_{P3}$–N, and $R_{P2}$–NH, simultaneously. When HCl did not exist in the solution, the theoretical isotherm was given by eq 28. When HCl existed in the solution, the theoretical equation was expressed by eq 41. The equilibrium coefficients for adsorption on each amino group were determined from the experimental data. The experimental $q_A$–$C_{TA}$ curve and $q_A$–pH curve were correlated by the theoretical equations reasonably well.

## Nomenclature

$C_0$ = initial concentration of L-glutamic acid in liquid phase, kmol/m$^3$

$C_{HCl}$ = equilibrium concentration of HCl in liquid phase, kmol/m$^3$

$C_{TA}$ = 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$^3$

$C_{A^\pm}$ = equilibrium concentration of $A^\pm$ 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$^3$

$C_{A^{2-}}$ = equilibrium concentration of $A^{2-}$ type of L-glutamic acid in liquid phase, kmol/m$^3$

$K$ = Langmuir equilibrium constant (eq 2), m$^3$/kmol

$K_1$ = 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$^3$

$K_{C,A}$ = equilibrium constant for adsorption of $A^\pm$ type of L-glutamic acid on primary ammonium group of chitosan fixed in PEI-CH (eq 19), m$^3$/kmol

$K_{C,HCl}$ = equilibrium constant for adsorption of HCl on primary ammonium group of chitosan fixed in PEI-CH (eq 34), m$^3$/kmol

$K_{P1,A}$ = equilibrium constant for adsorption of $A^\pm$ type of L-glutamic acid on primary ammonium group of PEI fixed in PEI-CH (eq 22), m$^3$/kmol

$K_{P1,HCl}$ = equilibrium constant for adsorption of HCl on primary ammonium group of PEI fixed in PEI-CH (eq 40), m$^3$/kmol

$K_{P2,A}$ = equilibrium constant for adsorption of $A^\pm$ type of L-glutamic acid on secondary ammonium group of PEI fixed in PEI-CH (eq 21), m$^3$/kmol

$K_{P2,HCl}$ = equilibrium constant for adsorption of HCl on secondary ammonium group of PEI fixed in PEI-CH (eq 36), m$^3$/kmol

$K_{P3,A}$ = equilibrium constant for adsorption of $A^\pm$ type of L-glutamic acid type on tertiary ammonium group of PEI fixed in PEI-CH (eq 20), m$^3$/kmol

$K_{P3,HCl}$ = equilibrium constant for adsorption of HCl on tertiary ammonium group of PEI fixed in PEI-CH (eq 35), m$^3$/kmol

$Q$ = total concentration of ammonium groups fixed in resin phase, kmol/m$^3$

$Q_A$ = saturation capacity of L-glutamic acid, kmol/m$^3$

$Q_C$ = concentration of primary ammonium group of chitosan fixed in PEI-CH, kmol/m$^3$

$Q_{P1}$ = concentration of primary ammonium group of PEI fixed in PEI-CH, kmol/m$^3$

$Q_{P2}$ = concentration of secondary ammonium group of PEI fixed in PEI-CH, kmol/m$^3$

$Q_{P3}$ = concentration of tertiary ammonium group of PEI fixed in PEI-CH, kmol/m$^3$

$q_A$ = equilibrium concentration of L-glutamic acid in resin phase, kmol/m$^3$

$q_{C,A}$ = equilibrium concentration of L-glutamic acid adsorbed on primary ammonium group of chitosan fixed in PEI-CH, kmol/m$^3$

$q_{C,HCl}$ = equilibrium concentration of HCl adsorbed on primary ammonium group of chitosan fixed in PEI-CH, kmol/m$^3$

$q_{P1,A}$ = equilibrium concentration of L-glutamic acid adsorbed on primary ammonium group of PEI fixed in PEI-CH, kmol/m$^3$

$q_{P1,HCl}$ = equilibrium concentration of HCl adsorbed on primary ammonium group of PEI fixed in PEI-CH, kmol/m$^3$

$q_{P2,A}$ = equilibrium concentration of L-glutamic acid adsorbed on secondary ammonium group of PEI fixed in PEI-CH, kmol/m$^3$

$q_{P2,HCl}$ = equilibrium concentration of HCl adsorbed on secondary ammonium group of PEI fixed in PEI-CH, kmol/m$^3$

$q_{P3,A}$ = equilibrium concentration of L-glutamic acid adsorbed on tertiary ammonium group of PEI fixed in PEI-CH, kmol/m$^3$

$q_{P3,HCl}$ = equilibrium concentration of HCl adsorbed on tertiary ammonium group of PEI fixed in PEI-CH, kmol/m$^3$

$V$ = volume of solution, m$^3$

$W$ = volume of wet adsorbent particles, m$^3$

$A^+$ = L-glutamic acid of $Ra-NH_3^+(-COOH)_2$

$A^\pm$ = L-glutamic acid of $Ra-NH_3^+(-COO^-)(-COOH)$

$A^-$ = L-glutamic acid of $Ra-NH_3^+(-COO^-)_2$

$A^{2-}$ = L-glutamic acid of $Ra-NH_2(-COO^-)_2$

$R_C-NH_2$ = primary ammonium group of chitosan fixed in PEI-CH

$R_{P1}-NH_2$ = primary ammonium group of PEI fixed in PEI-CH

$R_{P2}-NH$ = secondary ammonium group of PEI fixed in PEI-CH

$R_{P3}-N$ = tertiary ammonium group of PEI fixed in PEI-CH

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*Received for review* April 21, 1994
*Revised manuscript received* September 13, 1994
*Accepted* September 20, 1994[⊗]

IE940261F

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1994.