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Kinetic Study of the Extraction of Glutamic Acid by Naphthenic Acid in a Modified Lewis-Type Cell

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Kinetic Study of the Extraction of Glutamic Acid by Naphthenic Acid in a Modified Lewis-Type Cell

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Abstract

Due to the zwitterionic character, we may extract amino acids with ion-exchange carriers by controlling the pH of aqueous amino acid solutions. A modified Lewis-type cell experiment was conducted to study the extraction kinetics of glutamic acid by naphthenic acid, a cation-exchange carrier. The effects of agitation, interfacial area, carrier concentration, pH, and initial concentration of amino acid on the extraction rate were discussed. By comparison of the experimental results with the proposed interfacial extraction mechanism, it was found that the extraction equilibrium constant, K_{ex}, is 1.62×10^{-2}, the apparent forward extraction rate constant, k_1, is 0.63 cm⁴/mol·s, and the reverse rate constant, k_{-1}, is 38.9 cm⁴/mol·s. The intrinsic chemical reaction is controlled by the formation of an amino acid/carrier complex at the interface. The extraction mechanism proposed was successfully correlated with the experimental results.

Key Words: Extraction; Glutamic acid; Naphthenic acid; Kinetics; Modified Lewis-type cell

INTRODUCTION

The liquid membrane process was first developed (*1*) by using emulsions, and it has been applied to hydrometallurgy (*2–4*) hydrocarbon separation (*5–7*) wastewater treatment (*8–10*), and biomedical engineering (*11*, *12*). Recently, applications of emulsion liquid membrane (ELM) in biotechnology have become active (*13–15*). The ELM system has potential for the separation and concentration of amino acids (*16–18*).

The ELM system consists of an emulsion of two immiscible phases (usually water-in-oil, W/O) dispersed by mild agitation in a third, oil immiscible

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phase. This results in the dispersed interior phase being separated from the exterior continuous phase by a film of oil that acts as a "liquid membrane" between the two aqueous phases. The amino acid of interest can be transported from the exterior aqueous phase to the interior phase by a selective carrier which is incorporated into the oil membrane phase. Three types of carrier have been reported to be suitable for application in the amino acid transport systems. The first one is a positively charged lipophilic carrier, such as Aliquat 336, a kind of quaternary ammonium salt. The second one is a negatively charged carrier, such as di(2-ethylhexyl)phosphoric acid (D2EHPA), a kind of lipophilic acid. Both ionic carriers are complexed with counterions to maintain electroneutrality in the apolar membrane phase. These counterions can be exchanged with amino acid solute at the exterior phase/membrane interface by assuming the interfacial ion-exchange reaction forms a carrier/amino acid complex. The newly formed complex then diffuses across the membrane until it reaches the internal droplet. At the internal phase/membrane interface another ion-exchange reaction takes place. The counterion in the internal phase is exchanged for the amino acid which is then released into the internal phase. The newly formed carrier/counterion complex then diffuses back across the membrane to repeat the separation cycle. This transport mechanism is called countertransport.

The third type of carrier, the cotransport mechanism, is a neutral cyclic compound, such as crown ethers. In this kind of system the amino acid coupled with its counterion reacts simultaneously with the neutral carrier at the membrane interface to form a ternary complex. The formed complex then diffuses across the oil membrane, releases the amino acid salt, and the neutral carrier shuttles back to repeat the separation cycle. All the transport processes consist of an interfacial reaction step and a diffusion step. Therefore, it is necessary to know the interfacial kinetics to explain the transport rate quantitatively, especially when the diffusion rate is fast.

In the present work a cation-exchange carrier, naphthenic acid in cyclohexane, was used to extract glutamic acid. A rate equation based on an interfacial reaction mechanism is proposed. The proposed mechanism is discussed and correlated with experimental data obtained by using a modified Lewis-type cell.

EXPERIMENTAL

Naphthenic acid, average molecular weight 258, from Hayashi Pure Chemical Co., was used as the organic phase. It was dissolved in cyclohexane without further purification. Glutamic acid from Ferak Berlin was used to prepare the aqueous amino acid solution. The pH of the aqueous

solution was controlled by using HCl or KOH. All these reagents were of EP grade and were used as received.

The modified Lewis-type cell used in this study is shown in Fig. 1. Agitation of the liquids in the upper and lower compartments was performed by operating a conventional stirrer and a magnetically driven stirrer in opposite directions. The stirring speed was controlled at 130 rpm unless specially specified. The volume of the upper part for the organic solution was 500 mL and that of the lower part for the aqueous solution was 250 mL. The interfacial area between the two liquid phases was 31.4 cm^2. All experiments were carried out at 25°C as batch operations.

Samples of 0.5 to 1 mL were taken from the aqueous solution at scheduled time intervals. The glutamic acid content in the aqueous solution was determined by the ninhydrin reaction method. The concentration of amino acid in the organic phase was calculated by mass balance from the amino acid content of the aqueous phase. Equilibrium experiments were done separately by the bottle method.

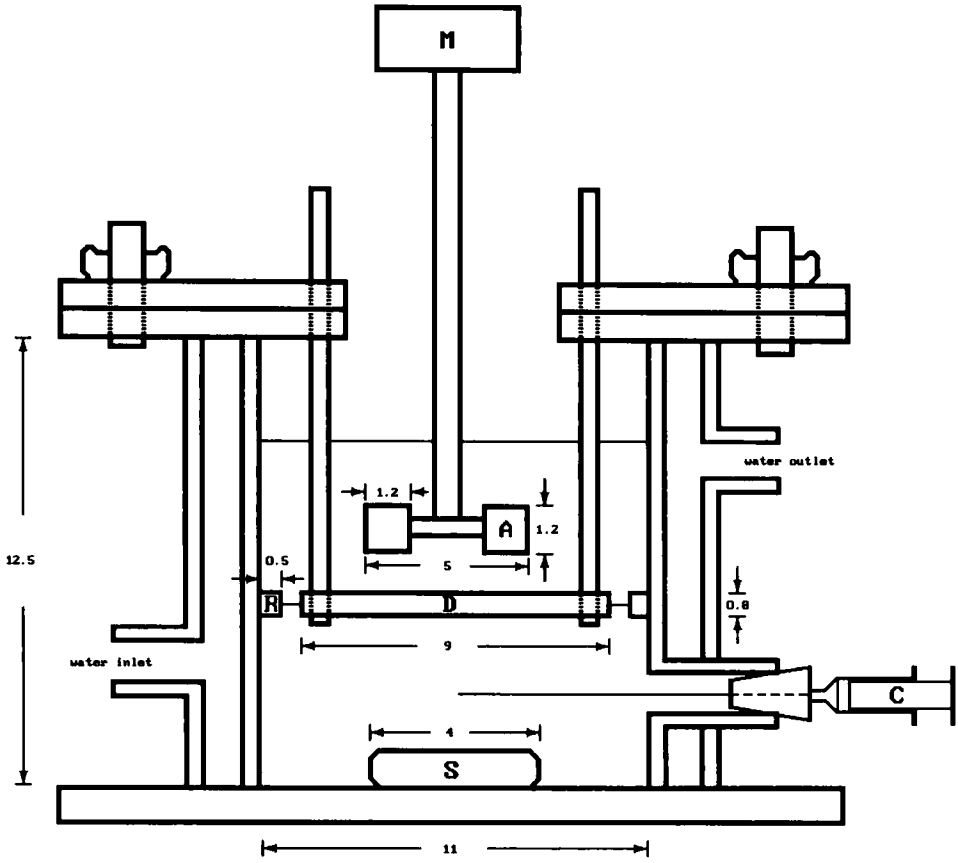
EXPERIMENTAL RESULTS AND DISCUSSION

The initial rate of amino acid extraction under various experimental conditions was obtained from the concentration change of amino acid in the aqueous solution with time in the initial period. That is, the initial rate of extraction across the interface was determined by

$$J_0 = -\frac{V_1}{S}\left(\frac{dC_1}{dt}\right)_{t=0}$$

Effect of Agitation Speed

The rate of liquid–liquid extraction in a stirred system can be controlled by both film diffusion processes and the kinetics of the chemical reactions taking place in the system. When the mass transfer rate is independent of the stirring speed of the two phases, a kinetic regime can be assumed, i.e., only chemical reactions are controlling the rate of mass transfer. The dependence of the agitation speed on the extraction rate is shown in Fig. 2. It was found that the extraction kinetics independent of the stirring rate are obtained when the speed is above 110 rpm. This indicates that the extraction rate occurs in a kinetic regime. However, as shown in Fig. 2, the interface becomes unstable when the speed is above 150 rpm. Therefore, a stirring speed of 130 rpm is used for most of the experiments.



material: acrylic
stirring speed: 130 rpm
interfacial area: 14.9 cm^2
unit: cm
A : six-bladed turbine
M : motor
C : syringe
R : O-ring
D : circle disc
S : magnetic stirrer

FIG. 1. Experimental apparatus (mass transfer cell).

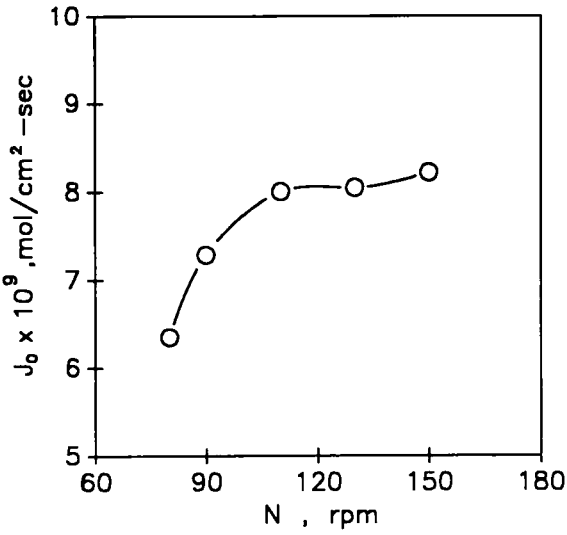


FIG. 2. Effect of stirring speed on the initial extraction flux. C_{10} = 0.1 M. $[\overline{MX}]_{20}$ = 0.15 M. pH = 1.44. S = 31.4 cm^2.

Effect of Interfacial Area

The rate of the liquid–liquid extraction process occurring in a kinetic regime can be controlled by either a homogeneous phase or interfacial chemical reactions. In the latter case a linear dependence must exist between the mass transfer rate and the interfacial area. Fig. 3 shows this kind of dependency. The conclusion can then be reached that the rate of extraction of amino acid in the present system is controlled by interfacial chemical reactions.

Effect of Carrier Concentration

Fig. 4 shows the effect of carrier on the initial extraction flux at a stirring speed of 130 rpm. It was found that the flux increases linearly with the carrier concentration.

Effect of Initial Concentration of Amino Acid

Fig. 5 shows the relation between the initial flux J_0 and the initial concentration of amino acid, C_{10}. It was found that J_0 is linearly proportional to C_{10}.

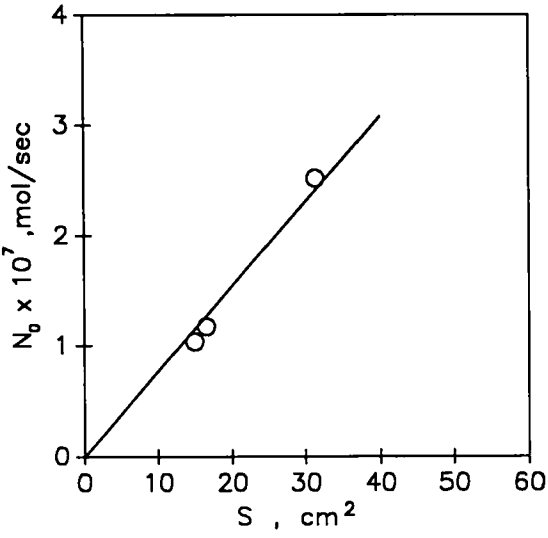


FIG. 3. Effect of interfacial area on the initial extraction rate. C_{10} = 0.1 *M*. $[\overline{MX}]_{20}$ = 0.15 *M*. pH = 1.44. *N* = 130 rpm.

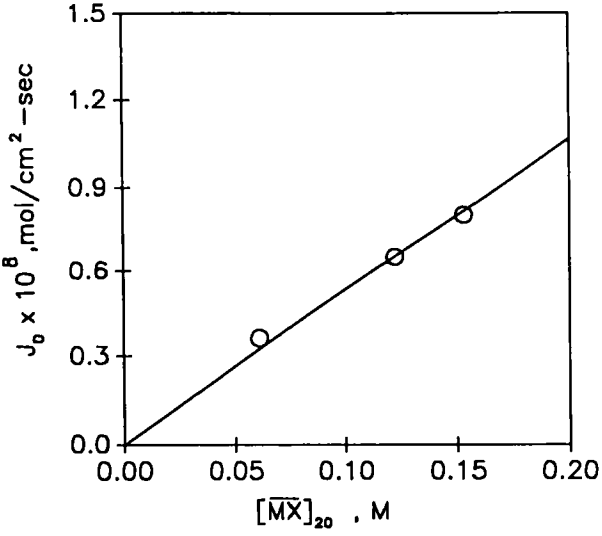


FIG. 4. Effect of carrier concentration on the initial extraction flux. C_{10} = 0.1 *M*. pH = 1.44. *S* = 31.4 cm^2. *N* = 130 rpm.

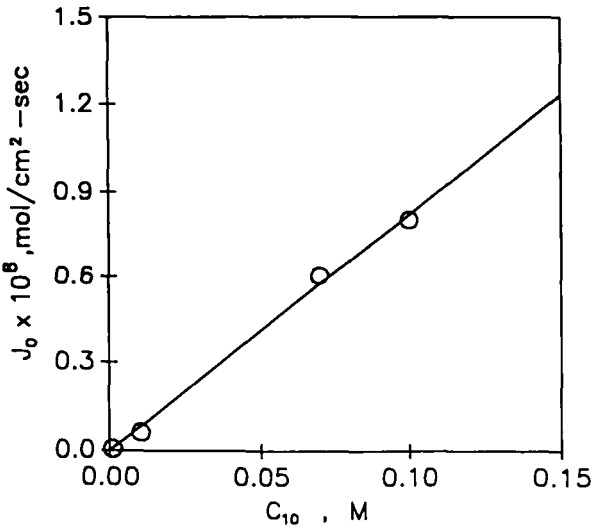


FIG. 5. Effect of initial amino acid concentration on the initial extraction flux. $[\overline{MX}]_{20}$ = 0.15 *M*. pH = 1.44. S = 31.4 cm^2. N = 130 rpm.

Effect of pH

Like all α-amino acids. glutamic acid is a zwitterion and its zwitterionic character imparts unique acid/base characteristics to the species:

$$\underset{pH < 2}{Glu^+} \overset{K_{a1}}{\underset{H^+}{\rightleftharpoons}} \underset{2 < pH < 4}{Glu^{+-}} \overset{K_{a2}}{\underset{H^+}{\rightleftharpoons}} \underset{4 < pH < 10}{Glu^-} \overset{K_{a3}}{\underset{H^+}{\rightleftharpoons}} \underset{10 < pH}{Glu^{2-}}$$

The effect of pH on the initial extraction flux is shown in Fig. 6. Apparently the flux is significantly higher for pH values below 3 in the system. This result is consistent with the zwitterionic character of glutamic acid.

Determination of Equilibrium Constant

The overall extraction of glutamic acid by a cation-exchange carrier, naphthenic acid, can be expressed as

$$A^+ + \overline{MX} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \overline{AX} + M^+, \qquad K_{ex} = \frac{k_1}{k_{-1}} = \frac{[\overline{AX}][M^+]}{[\overline{MX}][A^+]} \qquad (1)$$

where A^+ is an amino acid, $\overline{X}$ is an anionic carrier, and M^+ is the counterion of the ionic carrier. A plot of log ($[\overline{AX}]/[A^+]$) vs log ($[\overline{MX}]/[M^+]$) is shown

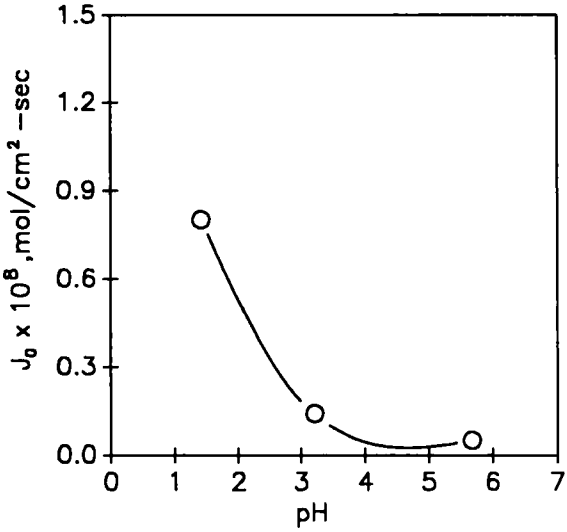


FIG. 6. Effect of pH on the initial extraction flux. $C_{10} = 0.1\ M$. $[\overline{MX}]_{20} = 0.15\ M$. $S = 31.4$ cm^2. $N = 130$ rpm.

as Fig. 7. The equilibrium constant, K_{ex}, which can be obtained from the intercept with the ordinate, is 1.62×10^{-2} for the glutamic acid/naphthenic acid system at 25°C.

KINETIC MODEL AND RATE EXPRESSIONS

Dissociation Equilibria of Amino Acids

Due to their zwitterionic character, amino acids have several ionic forms with various charges as a function of pH, say A^+, A, A^-, A^{2-}, according to the following dissociation equilibria:

$$A^+ \overset{K_{a1}}{\rightleftharpoons} A + H^+, \qquad K_{a1} = \frac{[A]_1[H^+]_1}{[A^+]_1} \tag{2}$$

$$A \overset{K_{a2}}{\rightleftharpoons} A^- + H^+, \qquad K_{a2} = \frac{[A^-]_1[H^+]_1}{[A]_1} \tag{3}$$

$$A^- \overset{K_{a3}}{\rightleftharpoons} A^{2-} + H^+, \qquad K_{a3} = \frac{[A^{2-}]_1[H^+]_1}{[A^-]_1} \tag{4}$$

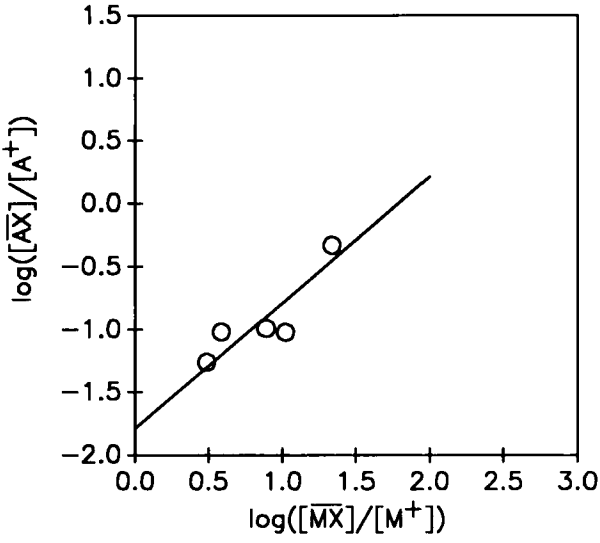


FIG. 7. Plot of log ($[\overline{AX}]/[A^+]$) vs log ($[\overline{MX}]/[M^+]$).

At 25°C, $K_{a1} = 6.46 \times 10^{-3}$, $K_{a2} = 5.62 \times 10^{-5}$, and $K_{a3} = 2.14 \times 10^{-10}$ for glutamic acid. Therefore, the total concentration of amino acid, C_l, in aqueous solution should be the sum of concentrations of all forms of amino acid. That is,

$$C_l = [A^+]_l + [A]_l + [A^-]_l + [A^{2-}]_l$$

$$= \left(1 + \frac{K_{a1}}{[H^+]_l} + \frac{K_{a1}K_{a2}}{[H^+]_l^2} + \frac{K_{a1}K_{a2}K_{a3}}{[H^+]_l^3}\right)[A^+]_l$$

$$= \sigma_+[A^+]_l \tag{5}$$

where

$$\sigma_+ = 1 + \frac{K_{a1}}{[H^+]_l} + \frac{K_{a1}K_{a2}}{[H^+]_l^2} + \frac{K_{a1}K_{a2}K_{a3}}{[H^+]_l^3} \tag{6}$$

By using Eq. (5), the concentration of A^+ can be estimated from the values of C_l and pH.

Extraction Kinetic Model

The experimental results of the extraction studies suggest an important role for the interfacial reaction in the extraction mechanism. Five consecutive steps constitute the amino acid extraction mechaniam:

1. The reactants, A^+ and $\overline{MX}$, diffuse from the bulk phases to the interface.
2. $\overline{MX}$ adsorbs on the interface.
3. $\overline{MX}$ reacts with A^+ at the interface to form $\overline{AX}$ and M^+.
4. $\overline{AX}$ desorbs from the interface.
5. The products, M^+ and $\overline{AX}$, diffuse back to the bulk phases.

Apparently, Steps 1 and 5 are diffusion processes and Steps 2 to 4 are interfacial reaction processes. To establish the model, the following interfacial reaction mechanisms are proposed:

$$\overline{MX} \overset{K_1}{\rightleftharpoons} \overline{MX}^*, \qquad K_1 = \frac{[\overline{MX}^*]_{2i}}{[\overline{MX}]_{2i}} \tag{7}$$

$$A^+ + \overline{MX}^* \underset{k'_{-2}}{\overset{k'_2}{\rightleftharpoons}} \overline{AX}^* + M^+,$$

$$r_2 = k'_2[A^+]_{1i}[\overline{MX}^*]_{2i} - k'_{-2}[M^+]_{1i}[\overline{AX}^*]_{2i} \tag{8}$$

$$\overline{AX}^* \overset{K_3}{\rightleftharpoons} \overline{AX}, \qquad K_3 = \frac{[\overline{AX}^*]_{2i}}{[\overline{AX}]_{2i}} \tag{9}$$

Among the interfacial reaction steps, Eq. (8) is the rate-determining step. By assuming that a linear adsorption isotherm expresses the adsorption and desorption steps, the interfacial extraction rate, r, of A^+ is obtained as follows:

$$r = r_2 = k'_2K_1[A^+]_{1i}[\overline{MX}]_{2i} - k'_{-2}K_3[M^+]_{1i}[\overline{AX}]_{2i}$$

$$= k_1\left([A^+]_{1i}[\overline{MX}]_{2i} - \frac{1}{K_{ex}}[M^+]_{1i}[\overline{AX}]_{2i}\right) \tag{10}$$

where

$$k_1 = k'_2K_1, \qquad k_{-1} = k'_{-2}K_3, \qquad K_{ex} = \frac{k_1}{k_{-1}} = \frac{K_1K_2}{K_3} \tag{11}$$

As mentioned before, the extraction mechanisms consist of diffusion steps and interfacial reaction steps. With the assumption of a pseudo-steady state, the extraction flux may be determined by

$$J = -\frac{V_1}{S}\frac{dC_1}{dt} = J_1 = r = J_2 = \frac{V_2}{S}\frac{d[\overline{AX}]_2}{dt} \tag{12}$$

where

$$J_1 = k_L([A^+]_1 - [A^+]_{1i}) = \frac{k_L}{\sigma_+}(C_1 - C_{1i}) \tag{13}$$

$$\begin{aligned} J_2 &= k_0([\overline{AX}]_{2i} - [\overline{AX}]_2) \\ &= k_0([\overline{MX}]_2 - [\overline{MX}]_{2i}) \\ &= k_M([M^+]_{1i} - [M^+]_1) \end{aligned} \tag{14}$$

Combining Eqs. (10)–(14) and eliminating the concentration of the species at the interface with the help of the mass balance equations,

$$V_1(C_{10} - C_1) = V_2([\overline{AX}]_2 - [\overline{AX}]_{20}) \tag{15}$$

$$[\overline{MX}]_{20} + [\overline{AX}]_{20} = [\overline{MX}]_2 + [\overline{AX}]_2 \tag{16}$$

$$V_1([M^+]_1 - [M^+]_{10}) = V_2([\overline{MX}]_{20} - [\overline{MX}]_2) \tag{17}$$

the overall extraction flux, J, is then obtained as

$$J = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \tag{18}$$

where

$$a = \frac{1}{k_M k_0 K_{ex}} - \frac{1}{k_0 k_L} \tag{19}$$

$$b = \frac{1}{k_1} + \frac{1}{\sigma_+ k_0}C_1 + \frac{1}{k_0 K_{ex}}[M^+]_1 + \frac{1}{k_L}[\overline{MX}]_2 + \frac{1}{k_M K_{ex}}[\overline{AX}]_2 \tag{20}$$

$$c = \frac{1}{K_{ex}}[M^+]_1[\overline{AX}]_2 - \frac{1}{\sigma_+}C_1[\overline{MX}]_2 \tag{21}$$

$$[M^+]_1 = [M^+]_{10} + C_{10} - C_1 \tag{22}$$

$$[\overline{MX}]_2 = [\overline{MX}]_{20} - \frac{V_1}{V_2}(C_{10} - C_1) \tag{23}$$

$$[\overline{AX}]_2 = [\overline{AX}]_{20} + \frac{V_1}{V_2}(C_{10} - C_1) \tag{24}$$

Substituting Eq. (18) into Eq. (12) and integrating numerically, the relation between the total concentration of amino acid, C_1, and time, t, is obtained. The initial extraction flux, J_0, can also be determined from Eq. (18) as follows:

$$J_0 = \frac{-b_0 + \sqrt{b_0^2 - 4a_0c_0}}{2a_0} \tag{25}$$

where

$$a_0 = \frac{1}{k_M k_0 K_{ex}} - \frac{1}{k_0 k_L} \tag{26}$$

$$b_0 = \frac{1}{k_1} + \frac{1}{\sigma_+ k_0} C_{10} + \frac{1}{k_0 K_{ex}}[M^+]_{10} + \frac{1}{k_L}[\overline{MX}]_{20} + \frac{1}{k_M K_{ex}}[\overline{AX}]_{20} \tag{27}$$

$$c_0 = \frac{1}{K_{ex}}[M^+]_{10}[\overline{AX}]_{20} - \frac{1}{\sigma_+} C_{10}[\overline{MX}]_{20} \tag{28}$$

Three limiting cases for the extraction model, each based on one rate-determining step, will now be discussed for comparison.

1. *Aqueous Phase Film Diffusion Controlled*

In this case, both the mass transfer coefficient in the oil phase, k_0, and the apparent interfacial reaction rate constant, k_1, are considered to be very large. Therefore, the extraction flux, J, can be simplified from Eq. (18) and becomes

$$J = k_L \frac{\left(\frac{K_{ex}}{\sigma_+} C_1[\overline{MX}]_2 - [\overline{AX}]_2[M^+]_1\right)}{\left(\frac{k_L}{k_M}[\overline{AX}]_2 + K_{ex}[\overline{MX}]_2\right)} \tag{29}$$

The initial flux for this case is

$$J_0 = k_L \frac{\left(\frac{K_{ex}}{\sigma_+} C_{10}[\overline{MX}]_{20} - [\overline{AX}]_{20}[M^+]_{10}\right)}{\left(\frac{k_L}{k_M}[\overline{AX}]_{20} + K_{ex}[\overline{MX}]_{20}\right)}$$

$$= \frac{k_L}{\sigma_+} C_{10} \qquad (\text{if } [\overline{AX}]_{20} = [M^+]_{10} = 0) \tag{30}$$

2. *Oil Phase Film Diffusion Controlled*

With the assumption of k_L, k_M, and k_1 very large, Eq. (18) is simplified to

$$J = k_0 \left\{ [\overline{MX}]_2 - \frac{[M^+]_1([\overline{MX}]_{20} + [\overline{AX}]_{20})}{[M^+]_1 + \frac{K_{ex}}{\sigma_+} C_1} \right\} \tag{31}$$

The initial flux will be

$$J_0 = k_0 \left\{ [\overline{MX}]_{20} - \frac{[M^+]_{10}([\overline{MX}]_{20} + [\overline{AX}]_{20})}{[M^+]_{10} + \frac{K_{ex}}{\sigma_+} C_{10}} \right\} \tag{32}$$

$$= k_0[\overline{MX}]_{20} \qquad (\text{if } [\overline{AX}]_{20} = [M^+]_{10} = 0) \tag{33}$$

3. *Interfacial Reaction Controlled*

In this case, the mass transfer coefficients k_L, k_M, and k_0 are all considered to be very large. Equation (18) is then simplified to

$$J = k_1 \left\{ \frac{1}{\sigma_+} C_1[\overline{MX}]_2 - \frac{1}{K_{ex}}[M^+]_1[\overline{AX}]_2 \right\} \tag{34}$$

The initial flux for this limiting case becomes

$$J_0 = k_1 \left\{ \frac{1}{\sigma_+} C_{10}[\overline{MX}]_{20} - \frac{1}{K_{ex}}[M^+]_{10}[\overline{AX}]_{20} \right\}$$

$$= \frac{k_1}{\sigma_+} C_{10}[\overline{MX}]_{20} \qquad (\text{if } [\overline{AX}]_{20} = [M^+]_{10} = 0) \tag{35}$$

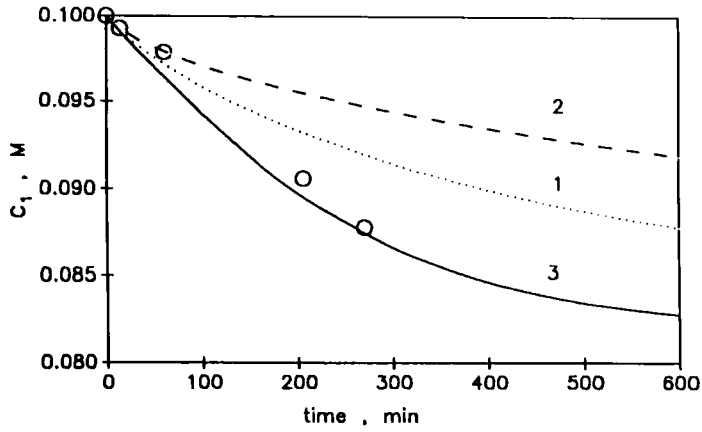


FIG. 8. Comparison of experimental results with the model calculations. (···) Aqueous phase controlled. (- -) Oil phase controlled. (——) Interfacial reaction controlled. $C_{10} = 0.1$ *M*. $S = 31.4$ cm^2. $N = 130$ rpm. $[\overline{MX}]_{20} = 0.15$ *M*. pH = 1.44.

From the experimental results, as shown in Figs. 2 and 6, it is believed that the systems considered in this study are controlled by interfacial chemical reactions. Therefore, Eq. (35) was used to analyze the experimental results of Figs. 4 and 5. The solid lines in these figures are the model calculations. The apparent forward reaction rate constant, k_1, correlated from these calculation results was found to be 0.63 cm^4/mol·s at 25°C. With $K_{ex} = 1.62 \times 10^{-2}$, the apparent reversed rate constant, k_{-1}, was then calculated to be 38.9 cm^4/mol·s.

For comparison, we applied Eq. (30) to calculate the aqueous phase mass transfer coefficient, k_L, and applied Eq. (33) to calculate the oil phase mass transfer coefficient, k_0. The values calculated for k_L and k_0 were 9.67×10^{-5} and 5.33×10^{-5} cm/s, respectively. A typical plot of the comparison of experimental data with the three limiting model calculations, based on the above correlated constants, is shown in Fig. 8. It again shows that the interfacial chemical reaction mechanism is in good agreement with the experimental results.

CONCLUSIONS

A study of the extraction kinetics of glutamic acid by a cation-exchange carrier, naphthenic acid, was carried out by using a modified Lewis-type cell. A rate equation involving the mass transfer terms and based on an interfacial reaction mechanism was derived. It was found that the limiting case, based on an interfacial chemical reaction rate-determining mecha-

nism, is in good agreement with the experimental results. The intrinsic chemical reaction is controlled by the formation of an amino acid/carrier complex at the interface.

NOTATION

A	amino acid zwitterion
A^+	positively charged amino acid
A^-	negatively charged amino acid
A^{2-}	negatively charged amino acid
a	constant defined by Eq. (19)
b	constant defined by Eq. (20)
c	constant defined by Eq. (21)
C	total concentration of amino acid in all form (mol/dm^3)
H^+	hydrogen ion
J	extraction flux (mol/cm^2·s)
K_1	equilibrium constant defined by Eq. (7)
K_2	equilibrium constant defined by Eq. (11)
K_3	equilibrium constant defined by Eq. (9)
K_{a1}	dissociation constant of amino acid (mol/dm^3)
K_{a2}	dissociation constant of amino acid (mol/dm^3)
K_{a3}	dissociation constant of amino acid (mol/dm^3)
K_{ex}	extraction constant defined by Eq. (1)
k_1	apparent forward rate constant defined by Eq. (11)
k_{-1}	apparent reverse rate constant defined by Eq. (11)
k_L	aqueous phase mass transfer coefficient of A^+ (cm/s)
k_M	aqueous phase mass transfer coefficient of M^+ (cm/s)
k_o	oil phase mass transfer coefficient of $\overline{MX}$ and $\overline{AX}$ (cm/s)
r	interfacial chemical reaction rate (mol/cm^2·s)
S	interfacial area (cm^2)
t	time (s)
V	volume (cm^3)
$[A^+]$	concentration of A^+ in aqueous phase (mol/dm^3)
[A]	concentration of A in aqueous phase (mol/dm^3)
$[A^-]$	concentration of A^- in aqueous phase (mol/dm^3)
$[A^{2-}]$	concentration of A^{2-} in aqueous phase (mol/dm^3)
$[\overline{AX}]$	concentration of $\overline{AX}$ in oil phase (mol/dm^3)
$[H^+]$	concentration of H^+ in aqueous phase (mol/dm^3)
$[M^+]$	concentration of M^+ in aqueous phase (mol/dm^3)
$[\overline{MX}]$	concentration of $\overline{MX}$ in oil phase (mol/dm^3)
σ_+	constant defined by Eq. (6)

Subscripts

0 initial condition
1 aqueous phase
2 oil phase
i interface

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