Mass Transfer Mechanism and Mathematical Model for Extraction Process of L-Theanine Across Bulk Liquid Membrane

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ABSTRACT: *This paper deals with the extraction of L-Theanine containing Aliquat 336 as a carrier and cyclohexane as solvent across bulk liquid membrane. The optimum operation condition are as follows: extraction time of 150 min, initial concentration of theanine in the feed phase is 1.8 g/L, the carrier concentration is 0.5 M, the ion of the receiving phase is 0.2 M NaCl of Na_2HPO_4-NaH_2PO_4 buffer solution. A mathematical model of transport process was deduced, the forward interfacial reaction rate constants and the backward interfacial reaction rate constants between the feed phase and the membrane phase, the receiving phase and the membrane phase were taken into account in the model equations. Using the experimental results, several parameters of the proposed model have been achieved by a nonlinear fitting method.*

KEY WORDS: *Extraction, Bulk liquid membrane, L-theanine; Model.*

INTRODUCTION

Over recent years, attention has been increased in the use of Liquid Membrane (LM) as selective separation barriers [1-4]. A LM achieves extraction through a higher affinity of the liquid membrane for a particular solute, it offers many advantages such as high selectivity, high efficiency of separation, high enrichment efficiency, minimum product contamination, low cost, no phase separation problem, easy scale up option for commercial applications and less use of the organic phase than in the classical solvent extraction process [5-8].

Recently, much attention has been focused on L-Theanine, a unique amino acid commonly found in green tea. It comprises 1-2 percent of the dry weight of tea leaves, makes up approximately 50 percent of the amino acids in tea, and is present as the free amino acid only-it does not occur in proteins [9]. L-Theanine is used as food additive and pharmacokinetics [10,11], and it can be produced by chemical synthesis [12], microbial fermentation [13,14] and extraction from the tea [15]. There are some disadvantages of chemical synthesis such as it is difficult to obtain materials, difficult to purify, easy to lead into contamination, and need to enantiosepation [10]. The method of microbial fermentation also has some disadvantages such as it is complicated to operate, difficult to scale up and need to carry on with purification [11,12]. Extraction L-Theanine from the tea is the most direct, effective and safe process. It concludes precipitation and ion exchange resin,

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but precipitation has some disadvantages such as low rate of extraction, complicated operation and leading into contamination of heavy metal ions [13], and the method of ion exchange resin also has some disadvantages such as complicated process of regeneration of ion exchange resin and decrease of extraction rate after regeneration [14]. So it is necessary to find a new process of more direct, effective and safe to separate L-Theanine from the tea.

In this work, a bulk liquid membrane was used to extract the L-Theanine and a mathematical model was presented for analyzing the transport of L-Theanine. It provides a new way to separate the L-Theanine and a simply mathematical model which can be easily used to simulate and predict the concentration of the L-Theanine of this mass transfer process.

THEORITICAL SECTION

In this paper we propose a mechanism for the transport of L-Theanine through BLM. The membrane consists of a carrier dissolved in a water immiscible organic solvent.

In order to simplify the mathematics and model development, the following assumptions are made:

1- An ideal system exists under complete mixing and constant temperature operation;

2- Constant physical and transport properties;

3- The membrane phase is completely immiscible with the aqueous phase;

4- The observed partition coefficient include (a) partition of the L-Theanine and (b) combination of the L-Theanine with the carrier.

Solute partition equilibrium

L-Theanine is a kind of amino acid, its extraction is complicated due to zwitterionic property. In this extraction process with Aliquat 336 ($R_3N^+CH_3$•Cl^-) as the carrier, the L-Theanine (H_2A) dissociates to A^- and H^+ first, then the ion-exchange reaction of A^- with $R_3N^+CH_3$•Cl^- at the interface of the feed phase and organic phase:

$$R_3N^+CH_3 \cdot Cl^-_{(m)} + A^-_{(f)} \leftrightarrow R_3N^+CH_3 \cdot A^-_{(m)} + Cl^-_{(f)} \quad (1)$$

The ion-pairing compound diffuses in the membrane phase, and reaches the interface of the membrane phase and receiving phase, then reacts with in the receiving phase to liberate $R_3N^+CH_3$•Cl^- and A^-:

$$R_3N^+CH_3 \cdot A^-_{(m)} + Cl^-_{(r)} \leftrightarrow R_3N^+CH_3 \cdot Cl^-_{(m)} + A^-_{(r)} \quad (2)$$

The A^- of L-Theanine transports from the feed phase to the membrane phase, then from the membrane phase to the receiving phase through the two processes. According to this transport mechanism, the concentration gradient of Cl^- is the driving force. The mass transfer process can be described as:

$$R_3N^+CH_{3(m)} + A^-_{(f)} \xleftarrow[k_{-1}]{k_1} \quad (3)$$

$$R_3N^+CH_3 \cdot A^-_{(m)} \xleftarrow[k_{-2}]{k_2} R_3N^+CH_{3(m)} + A^-_{(r)}$$

Where the subscripts “f” , “m” and “r” refer to the feed phase, the membrane phase and the receiving phase, respectively. k_1, k_2 and k_{-1}, k_{-2} refer to the forward interfacial reaction rate constants and the backward interfacial reaction rate constants, respectively.

Evaluation of mass transfer correlations

Three individual mass transfer resistances may be considered in this bulk liquid membrane process: the boundary layer resistance in the feed phase; the membrane resistance to solute diffusion across the membrane phase; the boundary layer resistance in the receiving phase. The concentrations of L-Theanine were directly measured in both feed phase and the receiving phase in the experiments, the corresponding molar quantity of L-Theanine in the membrane phase was established from the material balance, and the dimensionless molar fractions can be expressed as:

$$R_f = \frac{n_f}{n_{f0}} \qquad R_m = \frac{n_m}{n_{f0}} \qquad R_r = \frac{n_r}{n_{f0}} \quad (4)$$

Where n_{f0} refers to the initial molar quantity of L-Theanine in the feed phase, n_f, n_m and n_r are the molar quantities of L-Theanine in the feed, membrane and receiving phase, respectively. R_f, R_m and R_r represent the molar fractions of L-Theanine in the feed, membrane and receiving phase, respectively.

The flux of L-Theanine in each phase can be described as:

$$J_f = \frac{d_{R_f}}{dt} = k_{-1}R_m - k_1R_f \quad (5)$$

$$J_m = \frac{d_{R_m}}{dt} = k_1R_f + k_{-2}R_r - k_{-1}R_m - k_2R_m \quad (6)$$

$$J_r = \frac{d_{R_r}}{dt} = k_2 R_m - k_{-2} R_r \quad (7)$$

Because the concentration of Cl^- in the receiving phase is far larger than the concentration of L-Theanine, the effect of backward reaction of Eq. (2) on this extraction process can be neglected, that is, the backward interfacial reaction rate constants of k_{-2} can be neglected.

Integrating Eqs. (5) - (7), the molar fractions of L-Theanine in the feed, membrane and receiving phase will be expressed as:

$$R_f = \frac{k_1(\lambda_1 - k_2)}{\lambda_1(\lambda_1 - \lambda_2)}\exp(-\lambda_1 t) - \frac{k_1(k_2 - \lambda_2)}{\lambda_2(\lambda_1 - \lambda_2)}\exp(-\lambda_2 t) \quad (8)$$

$$R_m = \frac{k_1}{(\lambda_1 - \lambda_2)}\exp(-\lambda_1 t) - \frac{k_1}{(\lambda_1 - \lambda_2)}\exp(-\lambda_2 t) \quad (9)$$

$$R_r = \frac{k_1 k_2}{\lambda_1 \lambda_2} + \frac{k_1 k_2}{\lambda_1(\lambda_1 - \lambda_2)}\exp(-\lambda_1 t) - \frac{k_1 k_2}{\lambda_2(\lambda_1 - \lambda_2)}\exp(-\lambda_2 t) \quad (10)$$

Where λ is defined as:

$$\lambda_1 = \frac{1}{2}\left(k_1 + k_{-1} + k_2 + \sqrt{(k_1 + k_{-1} + k_2)^2 - 4k_1 k_2}\right) \quad (11)$$

$$\lambda_2 = \frac{1}{2}\left(k_1 + k_{-1} + k_2 - \sqrt{(k_1 + k_{-1} + k_2)^2 - 4k_1 k_2}\right) \quad (12)$$

Where J and t refer to the flux of the L-Theanine and the time, respectively. λ_1 and λ_2 are the defined constants which can be calculated by the interfacial reaction rate constants of k_1, k_{-1} and k_{-2}..

EXPERIMENTAL SECTIONS

Materials

L-Theanine was purchased from Xiyashiji Company, in China. Aliquat 336 was obtained from Xiyashiji Company, in China. the purity was above 99%.

The bulk liquid membrane vessel was self made up, its structure is shown in Fig. 1.

Analytical method

HPLC was performed with a LC-2010A Shimadzu system controller, a sample loop injector of 20 μL, a Shimadzu C-R3A Chromatopac.

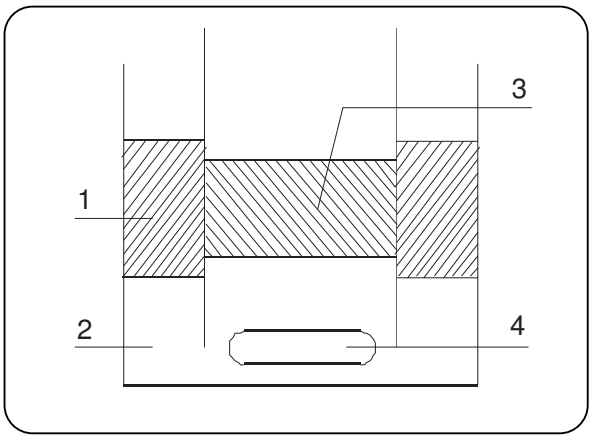

Fig. 1: Bulk liquid membrane separation vessel. 1. Receiving phase; 2. Organic membrane phase containing carrier; 3. Source phase; 4. Stirring bar.

Chromatographic conditions: [16] trifluoroacetic acid solution (pH 3.0) as mobile phase. The UV detection wavelength was set at 203 nm, flow rate 1 mL/min and room temperature.

Extraction of L-theanine

The experiments were carried out using Aliquat 336 as a chiral carrier in a membrane solvent (cyclohexane). The organic phase was prepared by adding Aliquat 336 (0.5 M) to cyclohexane. The aqueous feed solution was prepared by adding L-Theanine (0.01 M) to Na_2HPO_4-NaH_2PO_4 buffer solution of pH 12. The receiving phase was 0.2 M NaCl of Na_2HPO_4-NaH_2PO_4 buffer solution, its pH is the same as the feed solution.

The transport experiments were carried out under room tempreture, 30 mL feed phase and receiving phase solution, and 50 mL membrane phase solution were added into the bulk liquid membrane separation vessel. At various times, 100 μL samples were removed from the feed solution and the receiving solution and the L-Theanine concentrations were determined using HPLC.

RESULTS AND DISCUSSION

Selection of extraction conditions

Effect of initial concentration of L-Theanine on extraction efficiency

In this extraction process, the extraction efficiency, E is expressed as:

$$E = \frac{n_m}{n_{f0}} = \frac{n_{f0} - n_f}{n_{f0}} \quad (13)$$

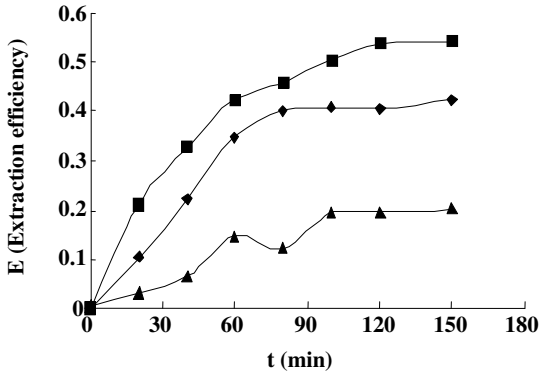

Fig. 2: Effect of initial concentration of L-Theanine on extraction efficiency. ■: initial concentration of L-Theanine is 1.8 g/L; ◆:2 g/L; ▲:1.4 g/L.

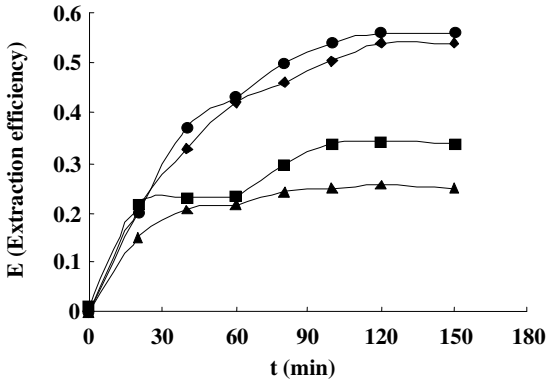

Fig. 3. Effect of carrier concentration in the membrane phase on extraction efficiency. ■: carrier concentration of 0.35 M; ▲: 0.25 M; ◆: 0.5 M;●: 0.65 M

The experimental data of extraction efficiency are shown by dot in Fig. 2. It can be seen that the extraction efficiency increase rapidly in the first few hours and then change slowly to reach equilibrium at about 120 min. It is because that the total mass transfer impetus is the highest one at the beginning since that the partition process is far from the equilibrium. For insuring the establishment of the extraction equilibrium, an extraction time of 150 min is used for the subsequent extraction experiments.

Fig. 2 also shows that the extraction efficiency increases with an increase of initial concentration of L-Theanine in the feed phase from 1.4 to 1.8 g/L, and then decreases from 1.8 to 2.0 g/L. The slope of the curve of 1.8 g/L is steeper than the slope for 1.4 and 2.0 g/L. This result can be used as a guideline to determine the optimum operation conditions for the extraction process.

Effect of carrier concentration in the membrane phase on extraction efficiency

As shown in Fig. 3, the extraction efficiency of L-Theanine is affected obviously by the concentration of Aliquat 336 in the membrane phase. The extraction efficiency increases with an increase of carrier concentration of Aliquat 336 in the membrane phase from 0.25 to 0.65 M, and it also can be seen that there is only a slightly increase for high concentration of the carrier from 0.5 to 0.65 M. So the optimum operation condition of the carrier concentration for the extraction process is 0.5 M according to the less use of the carrier.

Effect of ion concentration in receiving phase on extraction efficiency

NaCl dissolved in Na_2HPO_4-NaH_2PO_4 buffer solution was used as the ion of the receiving phase, its experimental data of extraction efficiency are shown by dot in Fig. 4. It can be seen that the extraction efficiency increases with an increase of Cl^- concentration in the receiving phase from 0.05 to 0.2 M, and then decreases from 0.2 to 0.3 M. The slope of the curve of 0.2 M is steeper than the slope for 0.05 and 0.3 M. So 0.2 M NaCl is selected as the suitable receiving agent.

Model simulation and transport kinetics

The transport kinetics of L-Theanine through the bulk liquid membrane with Aliquat 336 as the carrier and cyclohexane as the organic solvent was examined at 303.15 K. The experimental results are shown by dots in Fig. 5. It can be seen that R_f decreases monotonically with time and R_r increases monotonically with time oppositely, while R_m increases with time first and then decreases with time after it reaches a maximum.

There are there unknown constants of k_1, k_2 and k_{-1} in the mass transfer model. Using the experimental data of the molar fractions of L-Theanine in the feed, membrane and receiving phase which are shown by dots in Fig.5, the unknown parameters can be obtained by nonlinear fitting method as: $k_1 = 1.05\times10^{-2}$ (min^{-1}), $k_2 = 1.13\times10^{-2}$ (min^{-1}), and $k_{-1} = 9.5\times10^{-3}$ (min^{-1}). The simulation curves of the molar fractions are shown by line in Fig. 5.

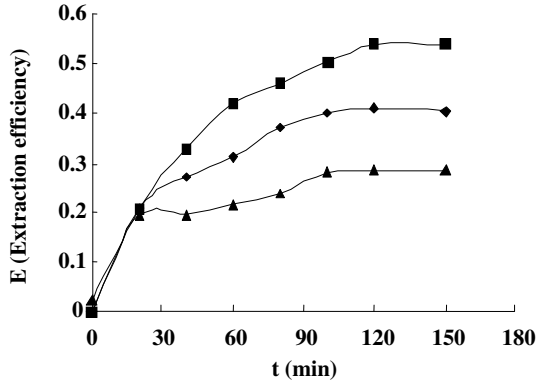

Fig. 4: Effect of ion concentration (Cl⁻) in receiving phase on extraction efficiency. ■: Cl⁻ concentration is 0.2 M; ◆:0.3 M; ▲:0.05 M.

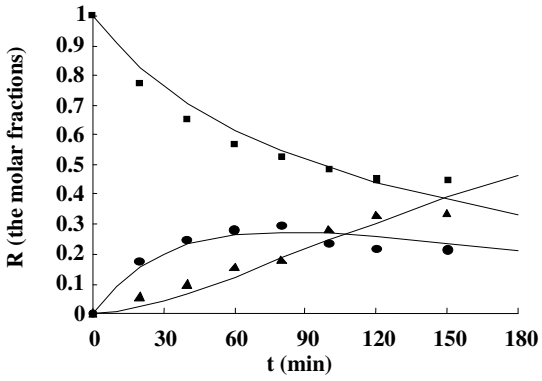

Fig. 5: Experimental data and model simulation of the molar fractions of L-Theanine in the feed (R_f, ■), membrane (R_m, ●) and receiving phase (R_r, ▲) at 303.15 K.

CONCLUSIONS

Extraction of L-Theanine containing Aliquat 336 as a carrier and cyclohexane as solvent across bulk liquid membrane was carried out successfully. The optimum operation condition are as follows: extraction time of 150 min, initial concentration of L-Theanine in the feed phase is 1.8 g/L, the carrier concentration is 0.5M, the ion of the receiving phase was 0.2M NaCl of Na_2HPO_4-NaH_2PO_4 buffer solution.

A mathematical model was developed to analyze the mass transfer process. The forward interfacial reaction rate constants and the backward interfacial reaction rate constants between the feed phase and the membrane phase, the receiving phase and the membrane phase were taken into account in the model equations. Using the experimental results of the solute concentration, several parameters of the proposed model had been achieved by nonlinear fitting method. It is a simply mathematical model which can be easily used to predict the concentration of this process.

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