Permeation of Phenylalanine through Polymer Inclusion Membrane Containing Bi-functional Ionic Liquid

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Phenylalanine, which is an essential amino acid, is used as a nutritional supplement. Development of a more effective separation technique from the broth is desired. We conducted permeation of phenylalanine through PVC-based membrane containing bi-functional ionic liquid consisting of Aliquat 336 and bis(2-ethylhexyl)phosphoric acid (D2EHPA), [A336][D2EHPA], as a carrier. Phenylalanine successfully permeated through PIMs containing [A336][D2EHPA]. The permeation rates through PIM containing [A336][D2EHPA] were higher than those using a conventional ionic liquid, Aliquat 336. From the experimental data, the overall mass transfer coefficients were calculated and the feed film resistance was found to control the permeation process in a flat-sheet permeation apparatus.

1. Introduction

Phenylalanine, which is an essential amino acid, is used as a nutritional supplement. Phenylalanine is mostly produced commercially by fermentation involving recombinant E. coli [1]. Ion exchange have been generally used for extracting amino acids from the fermentation broth. Development of a more effective separation technique is still required to extract and purify phenylalanine from the fermentation broth. A number of alternative processes for amino acid recovery have been proposed, including solvent extraction [2], adsorption [3], supported liquid membrane [4], electrodialysis [5] and aqueous two-phase extraction [6].

Recently, supported liquid membranes (SLM) based on ionic liquids (ILs) such as Aliquat 336 and Cyphos IL-101 have been proposed. However, the main problem for SLM operation is membrane instability caused by the loss of the membrane solution from the membrane pore [7].

In this study we applied the polymer inclusion membranes (PIMs) containing ILs to the separation of phenylalanine. PIMs are formed by casting a solution containing a carrier, a plasticizer and a base polymer to form a thin, flexible, and stable film. Their superior stability over SLMs has been reported [8]. Ionic liquid based on Aliquat 336 in this study was used because Aliquat 336 played roles of both carrier and plasticizer. However, permeation percent of phenylalanine through SLM including Aliquat 336 diluted in organic solvent is not so high (<50%) [7]. Therefore, we examined the bi-functional ionic liquid extractant based on Aliquat 336 as a carrier [9]. Aliquat 336-based bi-functional ionic liquid can be easily prepared by combining Aliquat 336 and acidic extractants such as organophosphorous extractants and carboxylic acid extractants by anion exchange reaction. The Aliquat 336-based bi-functional ionic liquid extractant has been applied to rare metal separation using solvent extraction and polymer inclusion membrane because of its advantages of high...
selectivity and extractability, good stability, good interfacial phenomena, and low consumption of acid and base [10,11]. Because both Aliquat 336 and organophosphorous compounds such as bis(2-ethylhexyl)phosphoric acid (D2EHPA) have been reported as amino acid extractants [2,15], in this study, we used bi-functional ionic liquid consisting of Aliquat 336 and D2EHPA, [A336][D2EHPA] as a carrier of phenylalanine.

2. Experimental

2.1 Chemicals

Aliquat 336, bis(2-ethylhexyl)phosphoric acid (D2EHPA) and other chemicals of analytical grade were used as received in this study. Bi-functional ionic liquid extractant [trialkylmethyl ammonium][bis(2-ethylhexyl)phosphate] ([A336][D2EHPA]) was synthesized according to the procedure shown in the previous paper [12]. The preparation scheme and structure of [A336][D2EHPA] are shown in Figure 1.

![Figure 1. Preparation scheme and molecular structure of [A336][D2EHPA].](image)

2.2 Membrane preparation

The PIM was prepared by the solution casting method. A polymer solution was prepared by dissolving the PVC (n=1100) and the ionic liquid, [A336][D2EHPA] or [A336][Cl], in 25 mL of tetrahydrofuran (THF). The solution mixture was stirred with a homogenizer and poured into a petri-dish. After evaporating the THF for 24 h at room temperature, the resultant PIM was typically obtained with an average film thickness of 345 ± 63 μm using a micrometer (Digimatic, Mitsutoyo, Tokyo). When examining the effect of the membrane thickness, we adjusted the amount of solution mixture. PIM including [A336][Cl] was prepared as a control membrane.
2.3 Permeation experiment

The PIM was sandwiched between two cells of the apparatus shown in our previous paper [13]. A membrane with an effective area, \( A \), of 50 cm\(^2\) was fixed in the apparatus. The feed solution was 5 mmol/dm\(^3\) of an aqueous phenylalanine solution without pH adjustment. Stripping solutions included 0.1 mol/dm\(^3\) of aqueous sodium carbonate solution. The transport experiment was initiated by adding 100 mL of each solution at 297 ± 1 K to their respective compartments. The stirring speed of the magnetic bar in each cell was controlled at 300 rpm. Samples from both solutions were withdrawn at regular time intervals. All experiments were duplicated and were reproducible with 5% as relative standard deviation. Phenylalanine concentrations in the samples were determined at 257 nm with UV spectrophotometer (Shimadzu UV2550).

3. Results and Discussion

Figure 2 shows the typical results of the time courses of phenylalanine concentration in the feed and stripping solutions using [A336][Cl] (71wt%) and [A336][D2EHPA] (50%). Phenylalanine was successfully permeated to the stripping phase against the concentration gradient in both cases. Although decrease in the phenylalanine concentrations in the feed phase are almost similar in both membranes, the stripping rate with [A336][D2EHPA] was found to be higher than that with [A336][Cl], suggesting that [A336][D2EHPA] had a superior stripping performance.

Generally, the permeation flux through a membrane is expressed by the following equation [4,14]:

\[
J = -\frac{V_f}{A} \frac{dC_f}{dt} = K_{ov} C_f
\]

where \( K_{ov} \) is the overall mass transfer coefficient through the membrane. \( C_f \) is the feed concentration of phenylalanine, \( V_f \) is the volume of the feed solution and \( A \) is contact area. Therefore,

\[
\ln \left( \frac{C_f}{C_{f,0}} \right) = -aK_{ov} t
\]

where \( a = \frac{A}{V_f} = 50 \text{ m}^{-1} \) is the specific area and \( C_{f,0} \) is the initial phenylalanine concentration in the feed. Figure 3 shows the typical plots in the initial stage based on Eq. (2) and their plots showed the good linearity. Overall mass transfer coefficients, \( K_{ov} \), were obtained from the slopes of the straight lines in Fig. 3.

Figure 4 shows the effect of ionic liquid on \( K_{ov} \). Evidently, values of \( K_{ov} \) increased with increase in contents of ionic liquid in the membranes in both ionic liquids and \( K_{ov} \) values in [A336][D2EHPA] were higher than those in [A336][Cl]. It was found that [A336][D2EHPA] is a better carrier than [A336][Cl].

The overall resistance to mass transfer \( 1/K_{ov} \) is considered to be the sum of membrane resistance \( 1/K_m \) and the feed boundary layer resistance \( 1/K_L \):

\[
\frac{1}{K_{ov}} = \frac{1}{K_L} + \frac{1}{K_m} = \frac{1}{K_L} + \frac{\delta}{P}
\]

where \( K_m \) and \( K_L \) are the mass transfer coefficients in the membrane and in the feed liquid boundary layer, respectively, \( \delta \) is the membrane thickness, and \( P \) is the permeability. Figure 5 shows the relation between the reciprocal of the overall resistance and membrane thickness (50 wt% of [A336][D2EHPA]) based on Eq. (3). Although overall resistance was proportional to membrane thickness in lactate permeation through PIM.
containing [A336][Cl] [13], in this study overall resistances were independent on the membrane thickness, suggesting that the membranes containing [A336][D2EHPA] had higher fluidity and the feed boundary layer resistances mainly contributed to the overall resistance.

Figure 2. Time-courses of concentrations of phenylalanine in feed and stripping phases (PIM included 71 wt% [A336][Cl] or 50 wt% [A336][D2EHPA]).

Figure 3. Determination of overall mass transfer coefficient based on Eq. (2).

Figure 4. Effect of ionic liquid on overall mass transfer coefficient.

Figure 5. Relationship between overall resistance and membrane thickness (50 wt% of [A336][D2EHPA]).
4. Conclusion

We conducted permeation of phenylalanine through PVC-based membrane containing bi-functional ionic liquid [A336][D2EHPA] as a carrier. Phenylalanine successfully permeated through PIMs containing [A336][Cl] and [A336][D2EHPA] as an ionic liquid. The permeation rates through PIM containing [A336][D2EHPA] were higher than those using conventional ionic liquid [A336][Cl]. From the experimental data, the overall mass transfer coefficients were calculated and, the feed film resistance was found to control the permeation process in this apparatus. We conclude that the PVC-based membrane process including [A336][D2EHPA] is promising for the separation of phenylalanine when a PIM was prepared in a hollow-fiber configuration, which has very large specific area and small feed film resistance compared to a flat sheet.

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