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Effects of the stripping solution concentrations on the separation degree in Donnan dialysis for binary systems of amino acids

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Abstract

Separation of amino acids by Donnan dialysis using an ion-exchange membrane was studied. Donnan dialytic experiments were carried out using a commercial anion-exchange membrane Neosepta AM-1 (in OH^- form), glutamic acid–alanine mixed solutions as the feeds, and sodium hydroxide solutions as the stripping ones. The amino acid fluxes were then measured. The initial concentrations of the two kinds of amino acids in the feed were equal, while the sodium hydroxide concentrations of the stripping solutions were widely varied. The glutamic acid flux was greater than that of alanine under all experimental conditions. The glutamic acid flux increased with the stripping solution concentration and was roughly constant in the region above a certain concentration. On the other hand, the alanine flux monotonically increased with the concentration of NaOH. The flux ratios of glutamic acid to alanine also varied with the concentration, but had maximum values. It was found that not too high concentration of NaOH was essential to separate the amino acids in the Donnan dialysis. An upper limit of the appropriate concentration of stripping solution, in which the flux ratio was greater than 100, became higher with the amino acid concentration in the feed.

Furthermore, the reason why the flux ratio decreased with the increasing stripping solution concentration was discussed.

Keywords: Ion-exchange membrane; Donnan dialysis; Amino acid; Separation; Stripping solution

1. Introduction

The separation method using ion-exchange membranes is expected to be applicable for separating amino acids. One of the reasons is that the amino acids can permeate through the ion-exchange membrane, since they are ampholytes which have positive or negative charge according to the pH of the solution, and their molecular weights, being roughly 100, are relatively low.

Electrodialysis is well known as a ionic separation method using ion-exchange membranes, and has been investigated for the amino acid separation. Martinez et al. [1] carried out electrodialytic experiments of an alanine solution, and measured the flux of alanine through cation- and anion-exchange membranes. Kikuchi et al. [2] carried out electrodialytic experiments for a mixed solution containing glutamic acid, methionine and lysine. They concluded that the separation among these three amino acids was possible by electrodialysis. Elisseeva et al. [3] were used electrodialysis for the separation of a mixed solution including glycine, sodium chloride and sucrose. They suggested that the separation could be done successfully in two steps. The first step was the demineralization at the limiting current density to minimize the glycine flux through the membranes. The second step was to separate glycine from sucrose at higher current density, obtaining a high glycine flux.

Donnan dialysis [4–13] is also an ionic separation method using ion-exchange membranes, in which ions cross through an ion-exchange membrane based on Donnan equilibrium principle [14]. The Donnan dialysis has the advantage of a simpler apparatus and no electric field input over electrodialysis. Although there have been many investigations of the Donnan dialysis, most of them have involved the permeation of inorganic ions [4–12].

In the author's previous paper [13], Donnan dialytic experiments for mixed solutions of amino acids were described. In those studies, the anion-exchange membrane, glutamic acid–phenylalanine or glutamic acid–alanine mixed solutions as feeds and sodium hydroxide solutions as stripping ones were used. For a wide concentration range of the amino acid in the feed, and for fixed concentration of sodium hydroxide in the stripping solution

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(50 mol m^{-3}), the fluxes of the respective amino acids were measured. In the high feed concentration region above 10 mol m^{-3}, the glutamic acid flux was over 100 times higher than that of the other amino acid, and it was found that the Donnan dialysis was applicable for the separation of the amino acids. On the other hand, below 10 mol m^{-3}, the amino acid fluxes varied in a complicated manner with the concentration, and below 1 mol m^{-3}, there was little difference between the fluxes of the two amino acids. Furthermore, after soaking the membrane in the solution of the same concentration as the feed in the Donnan dialysis, uptake of the amino acids into the membrane was also measured. In the high feed concentration region, the flux ratio of the two amino acids higher than 100 could be explained from the uptake. In the middle and low concentration regions, however, the variations in the amino acid flux could not be explained from the uptake. Based on these experimental facts, it was suggested that when the feed concentration was low, the ion-exchange reaction became slower, and the resistance of the process in which the amino acid moves from the solution to the membrane could not be ignored.

In the present study, Donnan dialytic experiments with the anion-exchange membrane for glutamic acid–alanine mixed solutions were carried out under the conditions of a wide concentration range of sodium hydroxide in the stripping solution. Glutamic acid and alanine were chosen as one of the acidic amino acids and one of the neutral amino acids, respectively. The flux of the respective amino acids and flux ratios of glutamic acid to alanine were measured, and the effect of the stripping solution concentration on the separation degree (the flux ratio) was then examined. Furthermore, the reason why the separation degree varied with the concentration of the stripping solution was discussed from the view point of the ion-exchange rate of the amino acid at the liquid–membrane interface.

2. Experimental

2.1. Membrane

A commercial anion-exchange membrane, Neosepta AM-1 (Tokuyama Corporation), was used. This membrane is homogeneous and consists of a styrene–divinylbenzene copolymer with a quaternary ammonium group. It has an ion-exchange capacity of 1.52×10^3 equiv. m^{-3} (1.72 mequiv. (g dry membrane)$^{-1}$) and thickness of 1.37×10^{-4} m in the Cl^- form. Its electric resistance is 1.3–2.0 Ω cm^2, and its burst strength is 0.3–0.5 MPa.

2.2. Amino acids

The amino acids used were L-glutamic acid (Glu) and L-alanine (Ala). The molecular weight (Mw), isoelectric point (pI) and pK_a of the amino acids are shown in Table 1 [15,16].

2.3. Donnan dialytic apparatus and procedure

The batchwise Donnan dialyzer is schematically shown in Fig. 1. It consisted of a membrane, two compartments made of acrylic resin and stirrers made of glass. The membrane was fastened between the compartments with silicone rubber gaskets, and had an effective area of 3.35×10^{-3} m^2. The temperature of the system was kept at 298 K using a temperature-controlled water bath. The stirring speed in both compartments was set to 1000 rpm. This is because above the stirring speed of 1000 rpm, as found in our previous study [9], no mass transfer resistance exists in the liquid film.

Table 1
Physical properties of amino acids used

Amino acid	Mw	pI	pK_{a1}	pK_{a2}	pK_{a3}
L-Glutamic acid	147.1	3.22	2.19	4.25	9.67
L-Alanine	89.1	6.00	2.34	9.69	

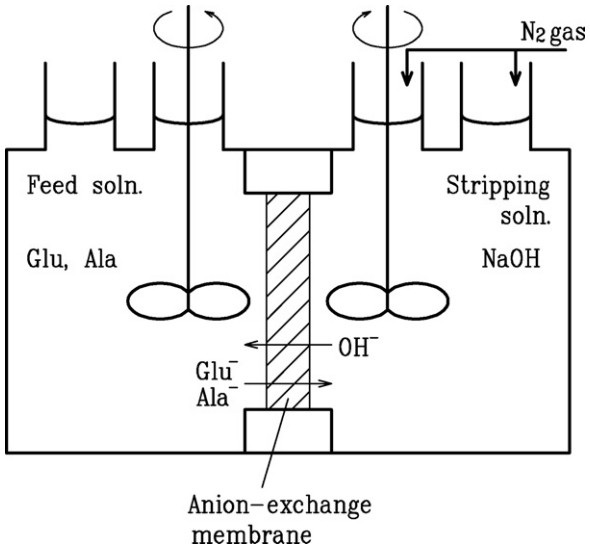

Fig. 1. Schematic diagram of Donnan dialyzer.

Prior to the Donnan dialysis, the membrane was converted into the OH^- form. The initial concentrations of the feed and stripping solutions are shown in Table 2. The feed solutions were glutamic acid solutions (Glu system) or glutamic acid–alanine mixed solutions (Glu–Ala system). In the Glu–Ala system, the initial feed concentrations of the two kinds of amino acids were equal. The sodium hydroxide solution of various concentrations was used as the stripping solutions. The two compartments were first filled with the feed and stripping solutions of a volume of 5.00×10^{-4} m^3 each and then the dialytic experiment began. At a specific interval of 10 min during the experiment up to

Table 2
Experimental conditions of feed and stripping solutions

Run number	Initial concentration (mol m^{-3})		
	Feed solution		Stripping solution
	Glu	Ala	NaOH
1	50.0	0.0	0–700
2	5.0	5.0	0–50
3	10.0	10.0	0–250
4	15.0	15.0	0–450