OPTICAL RESOLUTION OF α-AMINO ACIDS USING ENANTIOSELECTIVE MEMBRANES

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ABSTRACTS

Optical resolution of α-amino acid (tryptophan and tyrosine) optical isomers was achieved by a pressure driven membrane separation process, using self-supporting crosslinked membranes base on polysaccharide with different swelling indices that ranged from 100 to 70 %. The membranes prepared by casting and drying the polymer solution containing 5wt% acetic acid on an acryl plate followed by crosslinking with glutaraldehyde were characterized using such analytical methods as FTIR and swelling index measurements. On the way of separating the optical isomers, several experimental factors such as the concentration of the feed solutions, operating pressure and temperature, and degree of crosslinking of the membranes have been studied. When the chitosan membranes with 70 % of swelling index were used , almost complete optical resolution was obtained; 97.92 % of enantiomeric excess (ee %) and 2.26 $g/m^2 \cdot h$ of flux. The operating pressure and the concentration of feed solutions were respectively 1.0 kgf/cm^2 and 0.49 mmol/L.

INTRODUCTION

Nowadays, solid membrane separation process has naturally been considered as an attracting method for the optical resolution because of its several advantages such as ease of handling, instrumental simplicity and efficiency in energy as compared to the conventional methods, including preferential crystallization, chemical modification by an optical resolution agent, and high-performance liquid chromatography (HPLC) with a chiral stationary phase. Although there have been several reports on the optical resolutions through solid enantioselective membranes by Aoki. Et. al. and other groups.[2-10], solid membrane process for optical resolution is just on the beginning stage and has to be much more improved for them to be used for practical use.

The large content of chiral center is important factor for the formation of chiral environment in the membrane that is critical for the separation of optical isomers. Without chiral environment, it is almost impossible for the membrane to have enantioselectivity. In previous study, we tried sodium alginate, one of the polysaccharide containing anionic groups, to prepare enantioselective membranes for the separation of α-amino acids such as tryptophan and tyrosine, because it has excellent hydrophilicity and a large content of chiral centers in the backbone. Good enantioselectivity was measured.

Chitosan has a large content of chiral centers in the backbone likely to sodium alginate, but these polysaccharides have different backbone structure and different ionic group: chitosan has a cationic amide group, but sodium alginate an anionic carboxylic group. In this study, we have selected chitosan to prepare enantioselective membranes for the separation of -amino acids such as tryptophan and tyrosine. Likely to the sodium alginate, the excellent hydrophilicity and a large content of chiral centers of the chitosan seemed important for the membranes to have proper membrane properties for the separation of such water-soluble -amino acid isomers as tryptophan and tyrosine. Because of its excellent hydrophilicity, chitosan also has often been used for the formation of hydrophilic membranes

for the separation of water/alcohol or MTBE/methanol mixtures and showed good separation performances.[11-13]

Likely to the sodium alginate, chitosan membranes crosslinked with glutaraldehyde were prepared and used for the optical resolution of tryptophan and tyrosine, controlling the degree of crosslinking of the membranes, operating pressures and feed concentrations. The details of the results obtained are elaborated in this article.

EXPERIMENTAL

Membrane preparation

5 wt% chitosan solution in water was prepared by dissolving 5 g of chitosan into 1 kg of water containing 5wt% acetic acid at 50 °C. The chitosan solution was cast onto a polyester film attached to a glass plate, using a Gardner casting knife, and dried at room temperature in a fume hood for 4 days. After which, the dry chitosan films formed were peeled off the polyester film and immersed into an acetone solution containing 5.0 wt% GA and 1.0 wt% HCl for the crosslinking of the chitosan film. To control the degree of crosslinking of the chitosan films, the immersion time in the acetone solution was adjusted from 6 to 48 hrs. The crosslinked chitosan films were then taken out of the solution and washed out several times with an excess amount deionized water at 50 °C for 24 hours, and then dried under vacuum for 24 hours. The chitosan films prepared so were used as membranes. The thickness of the membranes was in the rage of 50 to 60 ㎛.

Swelling Index measurements

The swelling indices (SI) of the membranes were measured to compare the degree of crossliking of the membranes indirectly, using the following equation. The chitosan membranes crosslinked for different reaction time were fully swollen in deionized water at room temperature until there was no difference in the weight of the swollen membranes. After removing the water remained on the surface of the membranes, they were weighed to determine the weight of the swollen membranes (Ws). After which, they were dried under vacuum to a constant weight to determine the weight of the dried membranes (Wd).

$$SI = 100 \times (Ws - Wd)/Wd$$

Permeation tests

Flux for various racemic compounds (Flux, g/m^2h) were determined by weighing the permeated compound after the water had been evaporated.

$$Flux = Q/(At)$$

Where Q is the quantity of the solute permeated, t is the permeation time, and A is the area of the membrane. The composition (contents of D and L isomers) of the feed and permeates was measured by means of a liquid chromatography equipped with a Chiralpak-WH column (Diacel Chemical Industries, Ltd., Japan) as a optical resolution column, and a UV spectrophotometer (254nm) as a detector. The enantiomeric excess (ee) of permeates was determined from the peak areas of their two enantiomers, D- (A_D) and L-isomers (A_L).

$$\% ee = 100 \times (A_D - A_L)/(A_D + A_L)$$

The flux was determined by weighing the amounts of permeate penetrated through the membrane per unit time and unit membrane area.

RESULTS AND DISCUSSION

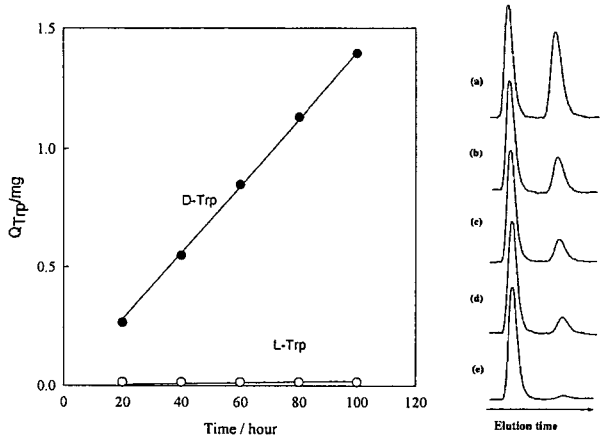

Figure 1. Characteristics of the optical resolution of tryptophan racemates using a chitosan membrane with 70 % of swelling index. The concentration of the feed solution and operating pressure were 0.49 mmol/L and 1 kgf/cm^2: (a) racemic Trp (feed); (b-e) Trp in the permeate at several SA membranes having different swelling indices from 100 to 70, respectively.

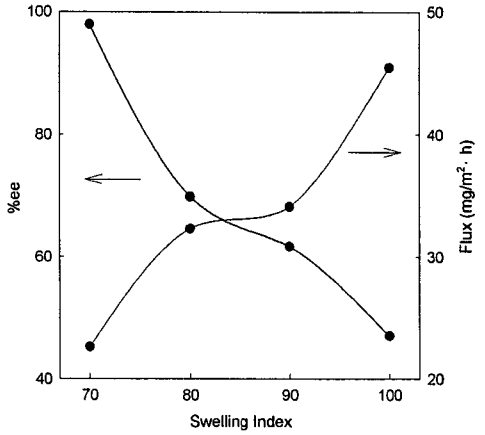

Figure 2. Characteristics of the optical resolution of tryptophan racemates as a function of the swelling indices of the chitosan membranes. The concentration of the feed solution and operating pressure were 0.49 mmol/L and 1 kgf/cm^2.

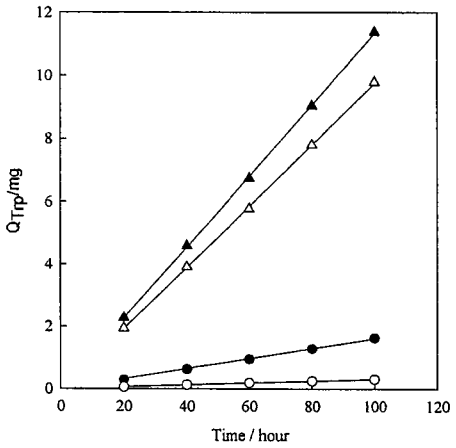

Figure 3. Effect of the concentration of the feed solutions on the characteristics of the optical resolution of tryptophan racemates, using a chitosan membrane with 80 % of swelling index: (●,○) Concentration of feed solution = 0.49mmol/L, (△,▲) Concentration of feed solution

= 4.9mmol/L; (●,▲) D-tryptophan, (○,△) L-tryptophan.

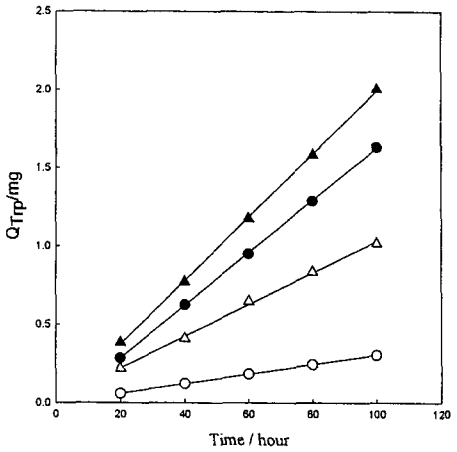

Figure 4. Effect of operating pressure on the characteristics of the optical resolution of tryptophan racemates, using a chitosan membrane with 80 % of swelling index: (●,○) Pressure = 1kgf, (△,▲) Pressure = 2kgf ; (●,▲) D-tryptophan, (○,△) L-tryptophan.

CONCLUSIONS

Enantioselective membranes based on polysaccharide crosslinked with GA are possible for the optical resolution of α-amino acids, especially tryptophan and tyrosine, by a pressure driven process. The presence five chiral carbons located on the ring structure of the polysaccharide seemed to make helical molecular structure and chiral environments in the membrane as cellulose and its derivatives did, making the membrane enantioselective. With increasing degree of crosslinking of the membrane was enabled to have better enantioselectivity by increasing the interaction between the functional groups of the chiral environment of the membrane and solutes penetrating through the membrane. The other factors that could decrease the intermolecular interaction between the membrane and solutes mentioned above, such as increase in operating pressure and increase in the concentration of a feed solution, and smaller size of solutes, acted against the enantioselectivity.

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