나노여과막의 Donnan이론을 이용한 모델 숙신산 용액으로부터 부산유기산들의 제거

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Removal of Byproduct Organic Acids from Model Succinate Solution by Donnan Theory of Nanofiltration Membranes

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1. Introduction

Some nanofiltration (NF) membranes can separate mono- and divalent ions in mixed electrolytes. Many researchers have reported such characteristics of NF [3, 5]. Especially, in the case of mixed-salts solutions with mono- and divalent anions, some NF membranes show a peculiar phenomenon such as negative rejection to monovalent anions. For example, Bowen and Gilron observed negative rejection of Cl ion by PES5 membrane in a mixed solution of NaCl/Na_2SO_4 and in a mixed solution of NaCl/sodium polyacrylate [1, 2]. These properties of NF can be applied for the separation of organic acids in fermentation industry.

Succinic acid and its derivatives are widely used as specialty chemicals for the production of polymers, surfactants/detergents, foaming agents, ion chelators, cosmetics, or food and health-related agents. Most succinic-acid-producing bacteria produce byproduct organic acids such as formate, acetate, and lactate.

In this study, nanofiltration (NF) was employed for the removal of byproduct organic acids from model succinate solution, considering that some NF membranes are much more permeable to monovalent anions such as formate, acetate and lactate than divalent anions such as succinate. Succinate was to be retained, while the byproduct organic salts were to be removed. Separation efficiency with the ratio of succinate to the other organic acid salts was also investigated and the results were interpreted based on the Donnan equilibrium theory.

2. Materials and Methods

Five commercial NF membranes, NF45, NF70, (Filmtec, Mineapolis, MN), NTR-729HF, ESNA1 (Hydranautics, Oceanside, CA) and TS-4040 (Trisep, Anahiem, CA) were tested. All experiments were carried out in a plate-and-frame type module with a filtration area of 60 cm^2. The membranes were rinsed with ultra-pure water before every run of experiment until an initial water flux was recovered. The membranes were simultaneously tested with two cells connected in parallel and the retentate and permeate were recycled for keeping feed concentration constant. The flux and rejection were measured at various pressures in the range of 50 to 300 psig. The feed temperature and circulation rate were 25 °C and 1.5 L/min, respectively.

Solution was made by mixing 0.3 M succinic acid (Sinyo, Japan), 0.1 M formic acid, acetic acid (Jusei, Japan), and lactic acid (Purac, Spain). During their mixing, the pH was adjusted to 7.0 by adding sodium hydroxide to this mixed solution. The composition of each component and pH of the solution were chosen by considering the composition of the general fermentation broth.

A high performance liquid chromatograph with a UV detector (Hitachi, Japan) at 210 nm and a HPX-87 column (BioRad, Richmond, CA) at 45 oC were used for the analysis of organic acids. The 8 mM sulfuric acid was used as the mobile phase at 0.6 L/min of flow rate.

3. Results and Discussion

3.1. Membrane selection

Membranes suitable for the purposeof this study must have a low rejection of monovalent anions and a high rejection of divalent anions as well as a high flux. Five NF membranes were tested by using four different 20 mM solutions of NaCl, $MgCl_2$, Na_2SO_4 and $MgSO_4$ at an operating pressure of 100 psig and a flow rate of 1.0 L/min. Solutions of poly-ethylene glycol's (PEG) with various molecular weights were also used for the identification of the nominal pore sizes of the membranes tested. Among the tested membranes, NF45 and ESNA1 showed large rejection differences between the monovalent anion, Cl- and the divalent anion, SO_4^{2-}. NF45 showed a salt rejection sequence: $MgSO_4$ > Na_2SO_4 > $MgCl_2$ > NaCl, and ESNA1 showed a salt rejection sequence: Na_2SO_4 > NaCl > $MgSO_4$ > $MgCl_2$. ESNA1 has a larger pore size than NF45 as evidenced by the experiments results with PEG solutions. ESNA1 showed a higher rejection to Cl ions (or NaCl) than NF45 even though it had a larger pore size. This implied that ESNA1 had a higher surface charge than NF45. Considering that the hydrated diameters of the ions involved are in the order: Mg^{2+} > SO_4^{2} > Na^{+} > Cl , it seemed that the Donnan equilibrium acted as the major factor on the ions transportation in the case of ESNA1, while the Donnan equilibrium and sieve effect simultaneously acted in the case of NF45 [4].

3.2. Separation of quaternary organic acid salts solutions

The quaternary organic acid salts solution wasprepared by the addition of 0.1 M of formate, acetate and lactate to a 0.3 M succinate solution and the rejections of each anion involved by NF45 and ESNA1 were measured at various fluxes. NF45 shows a relatively high rejection of succinate and low rejection of monovalent organic acid salts, as shown in Fig. 1. Especially, the rejections of formate and acetate showed negative values in the flux range tested. Such a pumping of certain components across the membrane in a mixed solution of charged molecules occurs due to the electro-neutrality with their counter ion. In the case of our system, sodium ion was the counter ion. Sodium ions can freely permeate through the membrane, since there is no repulsion between them and the negatively charged membrane. However, they cannot move across the membrane alone due to electoneutrality. They must be accompanied by anions. Under this circumstance, sodium ion has a tendency to permeate with other anions than succinate since transport of succinate is much more restricted due to the strong repulsion by the membrane. The pumping effect was found to be significant in the order: formate > acetate > lactate. This order agrees with the order of their sizes.

As shown in Fig. 2, ESNA1 showed a lower rejection of succinate and higher rejection of monovalent anions than NF45. It is because ESNA1 has higher membrane surface charge than NF45. Based on the Donnan theory for mixed electrolytes, the separation between mono- and divalent anions is good when the membrane has a low surface charge. Therefore this experimental result can be well explained by the Donnan theory.

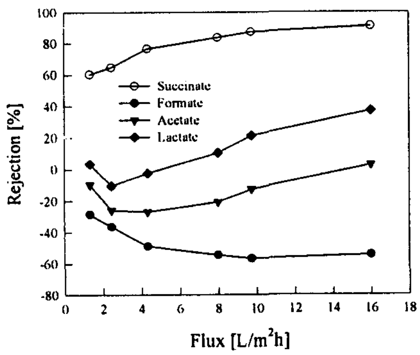

Fig. 1. Rejection of a mixed organic acid salts solution with 0.3 M sodium succinate and 0.1 M sodium formate, acetate and lactate by NF45 membrane as a function of flux

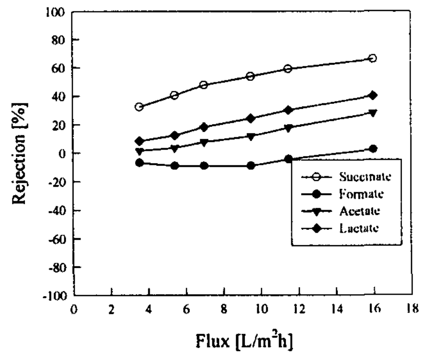

Fig. 2. Rejection of a mixed organic acid salts solution with 0.3 M sodium succinate and 0.1 M sodium formate, acetate and lactate by ESNA1-4040 membrane as a function of flux

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