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Pervaporation separation of water/ethanol mixture through tubular zeolite membranes

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1. Introduction

Utilization of biomass resources has considerable contribution to the reduction of carbon dioxide emission. Ethanol is one of the biomass products and is used as an additive to gasoline in several countries. Conventional process to produce ethanol involves energy-intensive azeotropic distillation. Pervaporation (PV) or vapor permeation (VP) is considered to be an alternative separation process to the conventional process. PV and VP separations became more efficient, viable as sophisticated fabrication techniques of inorganic zeolite membranes were developed. Some zeolite membranes for water/alcohol mixtures have been commercialized [1]. Zeolite membranes generally have high flux and high selectivity compared to polymeric membranes. However, fundamental data for zeolite membrane module under practical conditions are insufficient to save a lot of energy. It is one of crucial issues to obtain fundamental data to improve the entire separation process.

The final goal of our project is to obtain an optimum module design for removal of water from water/ethanol mixture by pervaporation or vapor permeation through hydrophilic zeolite membranes. As a step to complete the project, this study focused on two terms; concentration polarization at the membrane surface and estimation of water permeation flux based on limited experimental results. Pervaporation flux, mainly water flux, through a differential (short), tubular zeolite membrane as a function of process conditions such as feed flow rate, feed composition, and temperature was determined.

2. Experimental

Tubular zeolite-A membranes, supplied from BNRI Inc., with the length less than 20 cm were used for the pervaporation tests. Water/ethanol mixture was pervaporated through a tubular membrane at a fixed temperature from 70 to 120°C. Feed flow rate was from 0.5 to 15 L/min. Concentration of ethanol in the feed was above 88 wt.%. Permeated vapor was collected in a cold trap with liquid nitrogen. Flux was calculated from the weight of the collected vapor, the effective membrane area, and the measured period. The composition of the feed and permeate was determined using a gas chromatography (Shimadzu, GC-14B) to obtain selectivity, α, and flux for each component of water and ethanol.

3. Results and discussion

Zeolite-A membranes used in this study exhibited high water selectivity, α>6,000, as reported in the literature [1-3]. The total flux is nearly equal to the water flux. Therefore, the following sections deal only with water flux. Figure 1 shows water flux through a zeolite membrane as a function of feed flow rate at different temperature. Significant change in the water flux is seen at the feed flow rate less than 10 L/min. This feed flow rate corresponds to the Reynolds number more than 9,000. Therefore, even the Reynolds number is higher than 4,000, which is standard onset point of turbulent flow, we cannot always ignore the effect of boundary layer on the membrane surface on the water flux in this specific system. On the other hand, the water flux exhibits less change at the feed flow rate above 10 L/min, indicating that concentration polarization can be negligible at the high flow rate.

Figure 2 shows water flux through two membranes (#2 and #5) with different fabrication lots as a function of ethanol content in the feed. Water flux through the membranes decreases as the ethanol content in the feed becomes large; water content in the feed becomes small. The difference in the water flux between these two membranes is understandable since these membranes were prepared in different fabrication lots. However, we must notice a significant difference between these two membranes when the water flux is plotted against the difference in water activity between the feed and permeate as seen in Figure 3. The water flux through membrane #2 shows a linear relation with the activity difference while the water flux through #5 shows a curved line. The linearity, which is employed in the case of polymeric membranes, is widely accepted for zeolite membranes in the literature [4,5]. As far as the linearity can be obtained for a membrane like #2, estimation of the water flux at other conditions should be an easy task when concentration polarization can be ignored. On the other hand, a new permeation model is required to explain the non-linearity seen for membrane #5.

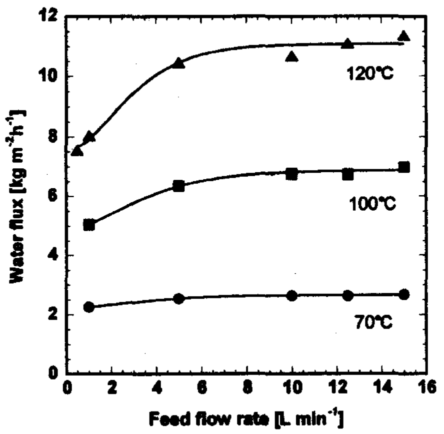

Fig. 1. Plot of water flux through zeolite-A membrane as a function of feed flow rate. Ethanol concentration in the feed was 90 wt.%.

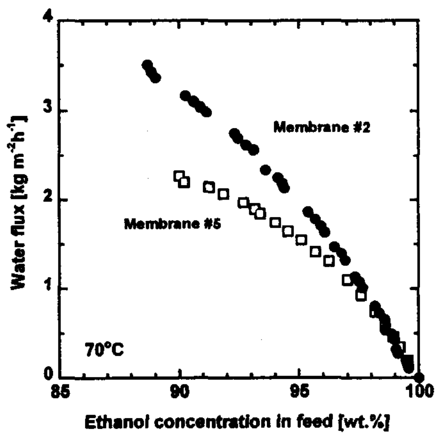

Fig. 2. Plot of water flux through zeolite-A membranes at 70°C as a function of ethanol concentration in the feed.

We propose a tentative model for water permeation through zeolite-A membranes to estimate water flux at other conditions as expressed by equation (1). The model expresses water flux with two different permeation modes; permeation based on surface diffusion (non-linear mode) and permeation based simply on activity difference (linear mode).

$$J = m_1\,exp(-m_2/RT)\,ln(1 + b_0\,exp(-\Delta H/RT)\Delta p) + m_3\Delta p \qquad (1)$$

Where J is the water flux, R the gas constant, T the temperature, b_0 the pre-exponential factor, ΔH the heat of adsorption, Δp the vapor pressure difference, and m_i the fitting parameters for the estimation. The fitting parameters contain values that are difficult to measure or obtain from the literature. Figure 4 shows an example of the fitting result for the division of water flux at 70°C into the two permeation modes. Extra pervaporation tests changing feed composition at 100 and 120°C were conducted. The fitting based on the model is applied to the obtained data, and then the fitting parameters were determined. Figure 5 shows the estimation results (solid line) along with experimental results (symbol). The estimated curves for water flux at 80, 90, and 110°C pass through the experimental plots, implying that the estimation process is reasonable. Figure 6 summarizes the estimation of water flux through the zeolite membrane as a function of temperature and ethanol content in the feed. Since industries use long tubular zeolite membranes or series modules leading to significant changes in the feed composition under practical pervaporation temperatures, the plot as seen in Figure 6 and the estimation process may provide valuable contribution to the optimum design of the zeolite membrane module for water/ethanol separation by pervaporation.

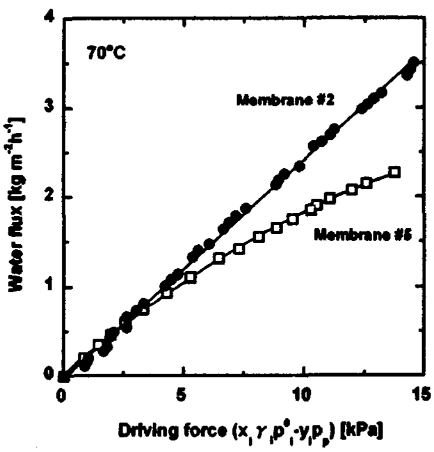

Fig. 3. Plot of water flux through zeolite-A membranes at 70°C as a function of driving force.

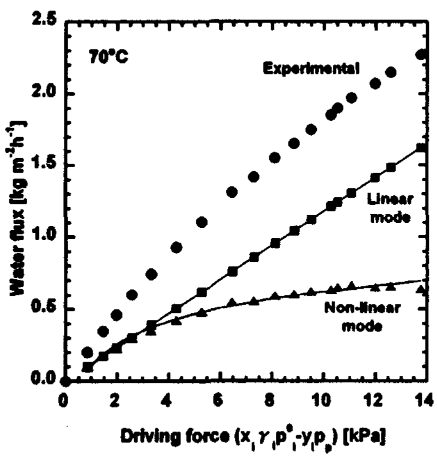

Fig. 4. Division of experimental results for water flux through zeolite-A membrane (#5) at 70°C into linear and non-linear permeation modes.

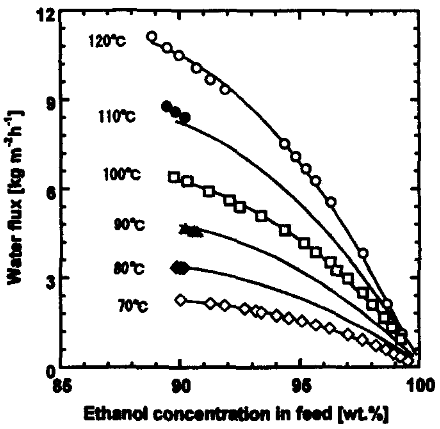

Fig. 5. Comparison of water flux as a function of ethanol concentration in the feed between experimental results and estimation results based on permeation model expressed by equation (1).

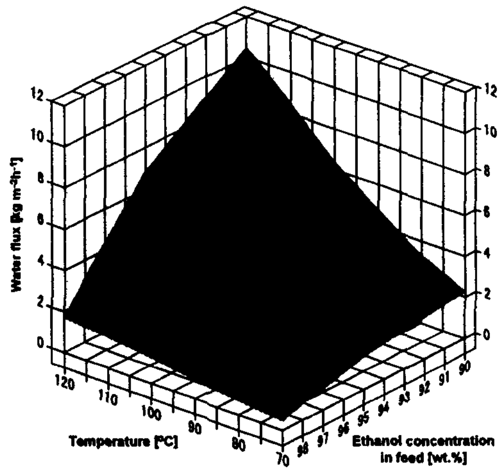

Fig. 6. Three-dimensional plot of calculated water flux through zeolite-A membrane as a function of temperature and ethanol concentration in the feed.

4. Conclusions

- Concentration polarization occurs when feed flow rate is low, leading to significant reduction of water flux through a zeolite-A membrane.
- Water flux under the conditions where concentration polarization can be ignored was successfully estimated at arbitrary conditions of temperature and feed composition.
- The estimation process based on experimental results from differential-type tubular zeolite-A membranes seems to be useful to obtain the optimum module design for practical use.

Acknowledgement

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