SEPARATION OF ETHANOL-WATER MIXTURE BY PERVAPORATION WITH ORGANIC COMPOSITE MEMBRANE: MODELLING OF SEPARATION PERFORMANCE USING MODEL PARAMETERS DERIVED FROM EXPERIMENTAL DATA

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Abstract

The permeation behavior of ethanol and water in pervaporation (PV) experiments using organic composite membrane; that is a polyvinyl alcohol (PVA) based active layer and a polyacrylo nitrile (PAN) supported layer was studied by measuring permeation flux and separation factor. The effects of permeate pressure (20-50 mbar), feed water concentration (5-1 wt%), and feed temperature (65-75 °C) were examined in this study. It was found that permeate pressure raised with reducing permeate flux and separation factor. Permeation flux enhanced and separation factor reduced with increasing feed water concentration and feed temperature. The solution-diffusion model that was derived by combination of Henry's law of sorption and Fick's law of diffusion was proposed to predict the solution-diffusion-desorption steps with a general driving force term and a permeation term. The activity coefficient of component in the ethanol water mixtures was calculated with UNIQUAC model. The solution-diffusion model was applied to predict the pervaporation flux through the PVA/PAN composite membrane. This model was successfully applied to the correlation of experimental results obtained with an organic composite membrane.

Keywords: Activation energy, Composite membrane, Pervaporation, Solution-diffusion model

Introduction

Pervaporation is a membrane process, in which a liquid mixture is brought in contact with a membrane at the upstream side and the permeate is removed as a vapor at the permeate side. The driving force for the process is established by reducing the relative pressure at the downstream side by either the use of an inert carrier gas or an applied vacuum. In pervaporation, a phase transition takes place as the feed is in a liquid state, whereas the permeate is obtained as a vapor [1]. Further downstream of the vapor is usually obtained as a liquid in a condenser.

The dehydration of organic solvents is the only application, in which pervaporation technology has so far been employed successfully on a full industrial scale. Currently more than ninety industrial units are in operation world-wide for the dehydration of ethanol, isopropanol, ethylacetate and multipurpose [2]. Most applications employ the hydrophilic PVA composite membrane which has been applied first by GFT Co., Ltd [3].

The combination of reactive distillation with pervaporation is favorable since global conversions close to 100% can be obtained with a reasonable size of the reactive section by

PVA based membranes. However, the evaluation of different options, pervaporation and vapor permeation, is needed for the development of an optimal design of the hybrid process. Moreover, the mathematical modelling should include the influence of the operational variables, since the temperature of the pervaporation feed is a variable which is essential influences membrane flux and therefore the design of the membrane unit [4].

Many models were proposed to predict the mass transfer process, such as solution-diffusion model, pore flow model, pseudo phase change solution-diffusion model, and etc. Among them, solution-diffusion model is most widely used in describing pervaporation transport including preferential sorption, diffusion and evaporation steps [5-7]. Modelling of the process of pervaporation is important not only for a quantitative understanding of the dependence of fluxes on the process parameter, but is also useful in design calculations for a pervaporation module and further optimization of the overall process [8].

In the present work, pervaporation experiments have been carried out to study the separation factor and mass transport flux of the system under varying operation conditions of permeate pressure, feed water concentrations and feed temperature. Based on the solution-diffusion theory, the permeation fluxes of ethanol and water through the composite membrane in the pervaporation process has been satisfactorily described.

Theory

The permeation flux through the membrane was calculated by the expression:

$$J_i = \frac{m_i}{At} \tag{1}$$

where J_i is the permeation flux of component i, g/m^2 h; m_i is the mass of component i in permeate, g; A is the effective membrane area, m^2 and t is the permeation time, h [9].
The separation factor, α is defined as follows:

$$\alpha = \frac{y_w / y_e}{x_w / x_e} \tag{2}$$

where y_w and y_e are the weight fractions of water and ethanol in the permeate and x_w and x_e are the weight fractions of water and ethanol in the feed, respectively [10]. The flux and separation factor are known to be more strongly dependent on the process conditions, possibly obscuring the driving force of the pervaporation process. The membrane permeance, Q can be directly calculated from the permeation flux, J as follows:

$$J_i = \frac{S_i D_i}{\delta}(p_{iF} - p_{iP}) = Q_i (p_{iF} - p_{iP}) = Q_i \Delta p_i \tag{3}$$

where Q_i is the permeance or pressure normalized flux which is composed of the sorption coefficient S_i (thermodynamic part) and diffusion coefficient D_i (kinetic part) of the component i in the membrane and the thickness of the membrane active layer δ. p_{iF} and p_{ip} are the pressure of component i in the feed (F) and permeate (p). The driving force of diffusion of component i, Δp_i can be considered either by the partial pressure, activity or chemical potential difference between upstream and downstream side of the membrane in pervaporation [11-12].

$$\Delta p_i = x_{iF}\, \gamma_i\, p_{iF}^{O} - y_{iP} p_P \quad (4)$$

This equation is identified with the relevant process parameters; feed temperature, feed concentration, and permeate pressure, p_P. The vapor pressure of the pure component i at feed p_{iF}^{O} in mmHg is calculated with the Antoine-equation [13] and it was converted to bar in this work.

$$\ln p_{iF}^{\circ} = \left(A - \frac{B}{t+C}\right) \quad (5)$$

where t is temperature in Celsius degree.

The activity coefficient γ of compound i in the mixture can be calculated with models such as UNIQUAC (UNIversal-QUAsi-Chemical), NRTL (Non-Random-Two-Liquid), Van Laar, Wilson, and etc. In this study, the activity coefficients for the binary systems: ethanol (i), water (j) was calculated using UNIQUAC model [14, 15]. MS Excel was used for the calculations. Table 1 presents the parameters used for the calculation of activity coefficients with UNIQUAC model and Antoine constants (A, B, C) for vapor pressure calculation. UNIQUAC model separates the activity of the solvent in the membrane into a combinatorial (C) and residual (R) parts [13]:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (6)$$

$$\ln \gamma_j = \ln \gamma_j^C + \ln \gamma_j^R \quad (7)$$

Activity coefficient for binary systems can be determined by:

$$\ln \gamma_i^C = \ln \frac{\varphi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\zeta_i}{\varphi_i} + \varphi_j \left(l_i - \frac{r_i}{r_j} l_j\right) \quad (8)$$

$$\ln \gamma_i^R = -q_i \ln\left(\zeta_i + \zeta_j \tau_{ji}\right) + \zeta_j q_i \left(\frac{\tau_{ji}}{\zeta_i + \zeta_j \tau_{ji}} - \frac{\tau_{ij}}{\zeta_j + \zeta_i \tau_{ij}}\right) \quad (9)$$

$$\ln \gamma_j^C = \ln \frac{\varphi_j}{x_j} + \frac{z}{2} q_j \ln \frac{\zeta_j}{\varphi_j} + \varphi_i \left(l_j - \frac{r_j}{r_i} l_i\right) \quad (10)$$

$$\ln \gamma_j^R = -q_j \ln\left(\zeta_j + \zeta_i \tau_{ij}\right) + \zeta_i q_j \left(\frac{\tau_{ij}}{\zeta_j + \zeta_i \tau_{ij}} - \frac{\tau_{ji}}{\zeta_i + \zeta_j \tau_{ji}}\right) \quad (11)$$

Where: l_i, parameter of component i $= \frac{z}{2}(r_i - q_i) - (r_i - 1)$

z , coordination number = 10

ζ_i, area fraction of component i $= \dfrac{q_i x_i}{\sum_j q_j x_j}$

φ_i, volume fraction of component i $= \dfrac{r_i x_i}{\sum_j r_j x_j}$

$$\tau_{ij}\text{, parameter of interaction between components i and j} = \exp\left(-\frac{A_{ij}}{R\,T}\right)$$

$$\tau_{ji}\text{, parameter of interaction between components j and i} = \exp\left(-\frac{A_{ji}}{R\,T}\right)$$

where A_{ij} and A_{ji} are UNIQUAC parameters between component i and j. q_i and q_j are molecular surface area for component i and j. r_i and r_j are molecular van der Waals volume for component *i* and *j*. UNIQUAC parameters are given in cal/mol with gas constant, R = 1.9872 cal/mol K and the temperature, T in K.

Table 1. Component Parameters used for the Calculation of Activity Coefficients and Vapor Pressure

Component	r	q	A_{ij}	A_{ji}	A	B	C
Ethanol	2.1055	1.972	-6.5974	319.8115	8.2371	1592.864	226.184
Water	0.95	1.4			8.1962	1730.630	233.426

The permeation fluxes depend on the temperature. The influence of the feed temperature on the permeance is described by the Arrhenius type relation [12]:

$$Q_i = Q_{i,ref} \exp\left[\frac{E_{Pi}}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T_F}\right)\right] \qquad (12)$$

The permeance of component i at the reference temperature T_{ref} = 60°C ($Q_{i,ref}$) and activation energy including the heat of adsorption and the activation energy for diffusion (E_{pi}) are calculated from experiment at various temperature. The mass transfer for pervaporation shown in the following equation is evaluated by combination the Equations (3, 4 and 12).

$$J_i = Q_{i,ref} \exp\left[\frac{E_{pi}}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T_F}\right)\right] . \left[x_{iF}\,\gamma_i\,\overset{\circ}{p}_{iF} - y_{iP}\,p_P\right] \qquad (13)$$

Experimental

Materials

For all experiments, an organic composite membrane with a polyvinyl alcohol (PVA) based active layer and a polyacrylo nitrile (PAN) as support layer was kindly supplied by GKSS Research Center Geesthacht GmbH, Germany. Analytical grade ethanol (EtOH) was provided by Vienna University of Technology, Austria.

Experimental Set-Up

The pervaporation experiments were carried out in a laboratory-scale unit supplied by Department of Thermal Process Engineering and Simulation, Vienna University of Technology (Austria) shown in Figure 1. The pervaporation module contains a rectangular flat sheet membrane with a membrane area of 0.0288 m^2. The prepared ethanol solvent mixture (2 liter) was fed into the tank, circulated with a pump through the membrane module and returned back to the tank. The permeate pressure at the downstream side was maintained within a range from 20 to 50 mbar and the feed temperatures were varied in the temperature range from 65 to 75°C which was controlled by thermostat. Pt-100 thermocouples were used to maintain the feed temperature T_F and retentate temperature T_R at the entrance and exit of the near module where also have feed pressure P_F and retentate pressure. The digital vacuum gauge which was installed in the vacuum line connecting the PV module and consider unit was used to monitor the vacuum pressure P_P. The permeate vapor was trapped in cool trap by liquid nitrogen. The trapped permeate was warmed up to room temperature and weighed. Throughout the PV experiment samples from liquid mixture in the feed vessel and permeate were drawn with a time interval of 1h and then the samples were analyzed with a DE45 Delta Range ^{TM} density meter. Process control and data acquisition were carried out using LabVIEW by National Instruments.

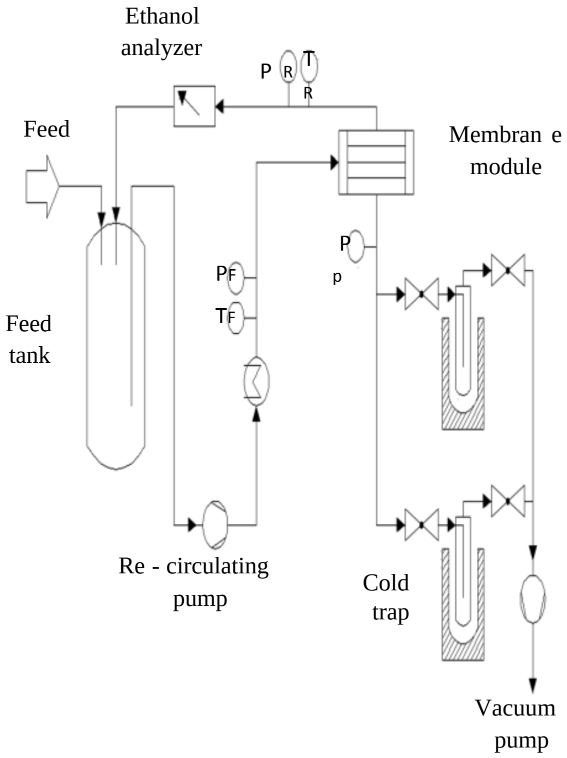
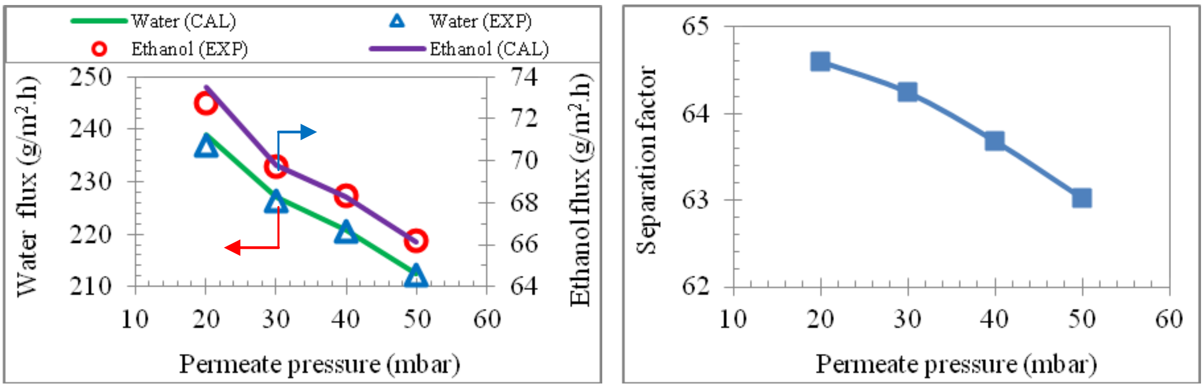


Figure 1. Pervaporation experimental set-up

Results and Discussion

Effect of Permeate Pressure

The effect of permeate pressure on the separation characteristic of the PVA/PAN composite membrane was investigated at feed water concentration (5wt%) and feed temperature (75°C). Four different permeate pressures of 20, 30, 40 and 50 mbar were considered to obtain uplifted fluxes and upraised separation factor. Figure 2, it can be observed the partial permeate flux and separation factor were declined when permeate pressure was enhanced from 20 to 50 mbar. These results indicate that flux is directly proportional to the driving force. The ethanol and water permeation fluxes predicted by Equation (13) are in fine aggrement with the experimental data. A permeate pressure of 20 mbar was selected to produce dehydrated ethanol by pervaporation based on the following given results.

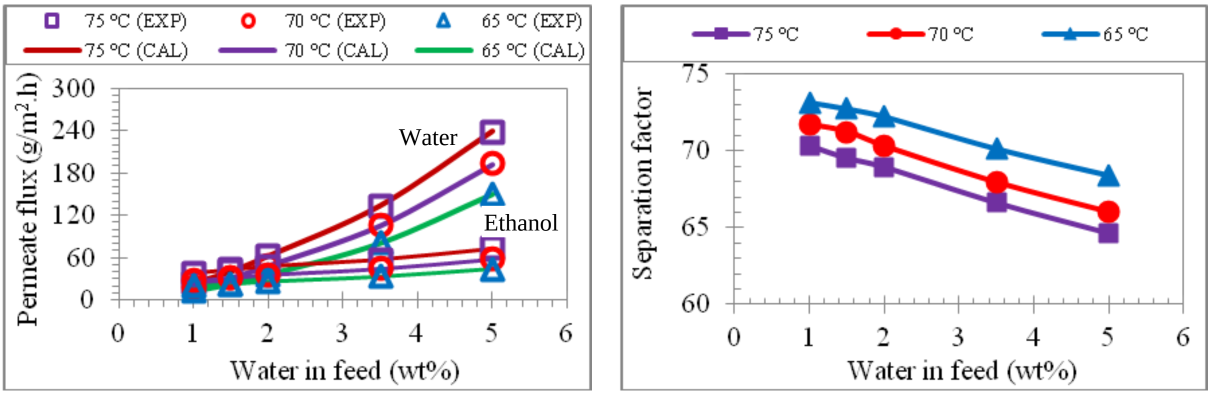


(a) (b)

Figure 2. Effect of permeate pressure on (a) experimental (EXP) and calculated (CAL) partial permeation fluxes (b) separation factor at feed water concentration (5wt%) and feed temperaure (75°C) with PVA/PAN composite membrane. The symbols are experimental data and the solid lines are calcualted values according to Equation (13)

Effect of Feed Water Concentration

Figure 3 shows the effect of feed water concentration change in the range from 1 to 5 wt% on permeation fluxes and separation factor. It was observed from the figure that the permeation flux of water is low at not only low water concentration values but also low feed temperature. The increase of water concentration in feed leads to slightly increase in ethanol permeation flux. The permeation flux of water showed a rapid increase from 24.23 $g/m^2.h$ to 236.98 $g/m^2.h$ at feed temperature (75 °C) while the separation factor declined, when the water concentration in feed increased from 1 to 5 wt%. This behavior is the influence of water: as feed water concentration enhances, the amorphous regions of the organic composite membrane take up more water and these results in a swelling of the membrane swollen. Due to the swelling of membrane the polymer chains become more flexible thus decreasing the energy which is required for diffusive transport through the membrane [16]. When feed water concentration was boosted, the partial permeation flux was upgraded.



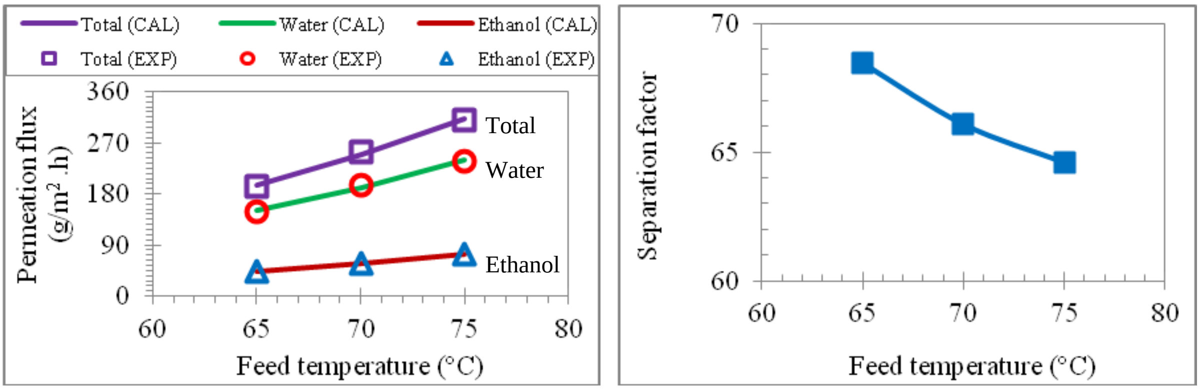
(a) (b)

Figure 3. Effect of feed water concentration on (a) experimental (EXP) and calculated (CAL) partial permeation fluxes (b) separation factor at different feed temperatures (75-65°C), and selected permeate pressure (20mbar) with PVA/PAN composite membrane.The symbols are experimental data and the solid lines are calcualted values according to Equation (13)

The permeation flux of water is much higher than the ethanol, which exhibits that the selected PVA/PAN composite membrane is preferentially perm-selectivity to water. Consequently, partial permeation fluxes increased with the increase of feed water concentration due to strong affinity between the polymer and water molecules. The sorption of water often results in swelling of the polymer matrix. In this case the ethanol permeation rate may be accelerated due to the plasticization of the polymer matrix, leading to the positive coupling effect. Therefore, the PVA/PAN composite membrane has lower selectivity at higher feed water concentration and this results in a decrease of separation factor. The permeation flux of ethanol and water predicted by Equation (13) are in pleasant aggrement with the experimental data as demonstrated in Figure 3(a).

Effect of Feed Temperature

The plot of permeation fluxes and separation factor against feed temperature at feed water concentration of 5wt% and selected permeate pressure of 20mbar are given in Figure 4. From Figure 4, it can be observed that total permeation flux enhanced from 192.71g/m^2.h to 309.72 g/m^2.h and separation factor decreased from 68.41 to 64.59, when the feed temperature was increased from 65°C to 75°C. These results can be explained: according to the free volume theory, the thermal motion of polymer chains in the amorphous regions randomly produces free volume. As temperature increase, the frequently and amplitude of the chain jumping increase and the resulting free volumes become larger. The diffusion rate of isolated permeating molecules and associated permeating molecules are high when the temperature is high, so that total permeation rate is high and the separation factor is low. This effect on the separation factor is shown in Figure 4(b) [16]. The permeation flux of ethanol and water predicted by Equation (13) are in fine aggrement with the experimental data.



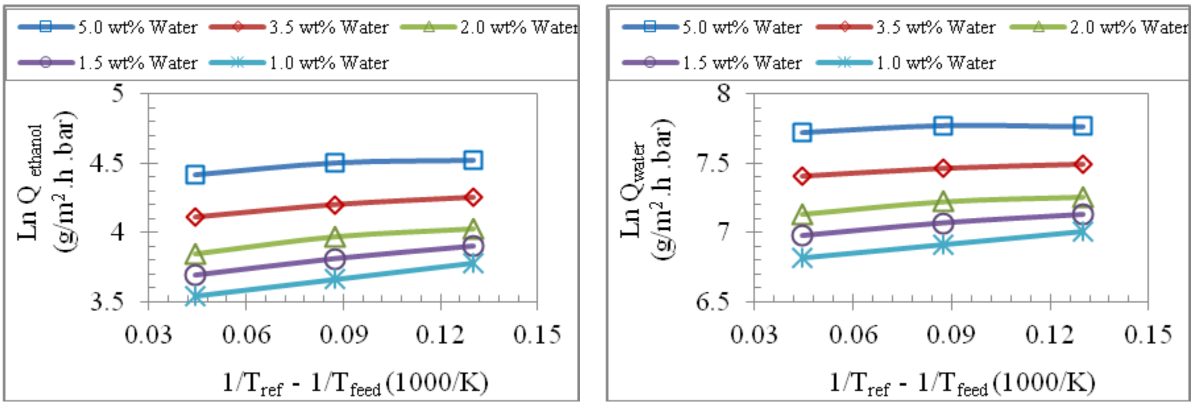
(a) (b)

Figure 4. Effect of feed temperature on (a) experimental (EXP) and calculated (CAL) permeation fluxes (b) separation factor at feed water concentration (5wt%), and selected permeate pressure (20mbar) with PVA/PAN composite membrane. The symbols are experimental data and the solid lines are calcualted values according to Equation (13)

The constants $Q_{i,ref}$ and E_{pi} were calculated from Equation 12 by plotting $\ln Q_i$ against the reciprocal temperature of different feed temperature (the slop = E_{pi}/R and the intercept

= $Q_{i,ref}$). Both the ethanol and water permeance follow an Arrhenius function indicated by the nearly straight line in Figure 5. The partial permeance, Q_i and the activation energy of ethanol permeation (E_e) and water permeation (E_w) are presented in Table 2. It can be seen that the activation energies of ethanol and water were declined as feed water concentrations were increased. The E_e are higher than E_w due to being the lower affinity between ethanol and PVA/PAN organic composite membrane than the affinity between water and membrane [10]. When the temperature was increased, the permeability of ethanol was higher than that of water and results in higher E_e and decrease of separation factor.

The activation energy of permeation (E_{pi}) is the sum of the activation energy of diffusion (E_D) and the enthalpy of dissolution (ΔH) of the permeant in the membrane. While E_D is generally positive, ΔH is usually negative for the exothermic sorption process. When the positive (E_D) dominates over the negative value of ΔH, positive value of E_{pi} occurs [17]. The positive values of ethanol permeation (E_e) and water permeation (E_w) in this study indicate an increase of membrane permeability coefficient with raising temperature.



(a) (b)

Figure 5. Effect of feed temperature on permeance of ethanol (a) and water (b) at feed water compositions and selected permeate pressure 20 mbar with PVA/PAN composite membrane

Table 2. Permeance and Activation Energy of Permeation for Ethanol and Water at Different Feed Water Concentration

Water Content in Feed (wt%)	**Permeance, Q (g/ m^2.h.bar)**		**Activation Energy of Permeation, E_p (kJ/mol)**	
	Ethanol	Water	Ethanol	Water
5.0	92.8	2377.2	10.0	4.0
3.5	70.6	1794.0	13.5	8.0
2.0	56.5	1431.8	17.3	12.4
1.5	49.6	1254.3	20.0	15.1
1.0	43.7	1104.2	23.0	18.7

Conclusions

The separation of ethanol water mixture with a PVA/PAN composite membrane was examined at various operating conditions such as permeate pressure, feed water concentration, and feed temperature. In the proposed model, solution-diffusion model and

UNIQUAC model are employed to describe the permeation flux. The experimental and predicted permeation fluxes increased with increasing feed water concent and feed temperature and decreasing with permeate pressure. The experimenal data of permeation fluxes based on the effects of feed pressure, feed water concentration and feed temperature are in good aggremnet with the calculated values using the solutioin-diffusion model. The permeance of both ethanol and water increased with incresaing feed water concentration due to the increase of driving force for the transport of water and ethanol. The permeance of water could be higher than that of ethanol because sorption of water increased with feed water concentraion. Permeation activities of ethanol and water decline with acceleration of water in feed. Permeation activity of ethanol would be higher than that of water because the affinity between water and organic composite membrane is stronger than between ethanol and organic composite membrane.

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