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Short Communication

PLASTICIZATION OF CHITOSAN MEMBRANE FOR PERVAPORATION OF AQUEOUS ETHANOL SOLUTION

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Abstract – The process of pervaporation in which two components diffuse through a nonporous polymer membrane was modelled when one of the penetrants can exert a plasticization action to the membrane material. Thereat a phenomenological model was employed for describing the plasticization effect on the diffusivities for penetrants in the membrane. The sorption equilibria and permeation fluxes for aqueous ethanol solutions in a chitosan membrane were measured, and the permeation fluxes for water were compared with those predicted by the proposed model. The concentration of sorbed water was linear with its weight fraction (x_A) in the feed solution, whereas the permeation flux of water was affected by the plasticization action of sorbed water to the polymer. This plasticization effect on the diffusion process can be simulated in terms of the proposed phenomenological model.

Key words: Plasticization, Chitosan, Membrane, Pervaporation

INTRODUCTION

The development of the membrane separation process necessitates the module and process design as well as the development of membrane materials. Intensive studies have been done toward the development and optimization of membrane materials. At the same time, more work should be done on rational design of membrane module and process. For the design purpose, the governing equations reflecting the transport phenomena in the membrane process must be determined. For the pervaporation and vapor permeation processes, a plasticization effect of penetrants on the polymer membrane should be incorporated into the transport equations. Thereat, the diffusion coefficients for penetrants can not be assumed to be constant across the membrane, but the concentration dependence of the diffusion coefficient must be taken into account, according to molecular or phenomenological models.

In the present work, the pervaporation behavior for aqueous ethanol solutions in prepared chitosan membranes was investigated by measurements of the sorption equillibria and permeation fluxes of respective components. The permeation fluxes of water were determined at various weight fractions of water in the feed solution and downstream total pressures, and compared with the predictions based on a phenomenological model proposed here.

RATE EXPRESSIONS IN PERVAPORATION

In the process of pervaporation wherein two components A and B diffuse through a nonporous polymer membrane, the diffusion flux for each component can be described as [Rautenbach and Albrecht, 1985]

$$J_A = -D_A \frac{dC_A}{dx} = -D_{A0}\ \exp(\kappa_{AA} C_A + \kappa_{AB} C_B)\frac{dC_A}{dx} \tag{1}$$

$$J_B = -D_B \frac{dC_B}{dx} = -D_{B0}\ \exp(\kappa_{BB} C_B + \kappa_{BA} C_A)\frac{dC_B}{dx} \tag{2}$$

like gas permeation in polymer membrane [Zhou and Stern, 1989]. Here, the diffusion coefficient for each component is assumed to depend on the concentrations of both components in the membrane because of the plasticization action of both components to the polymer.

Only component A exerts the plasticization action to the diffusion process, so that the diffusivities of components A and B can be simplified into

$$D_A = D_{A0}\ \exp(\kappa_{AA} C_A) \tag{3}$$

$$D_B = D_{B0}\ \exp(\kappa_{BA} C_A) \tag{4}$$

The diffusion flux of component A(water) can be written as

$$J_A = -D_{A0}\ \exp(\kappa_{AA} C_A)\frac{dC_A}{dx} \tag{5}$$

Accordingly, integration of Eq. (5) with J_A constant under the steady state leads to

$$J_A = \frac{D_{A0}}{\kappa_{AA}\,\delta}\left[\exp(\kappa_{AA} C_{A2}) - \exp(\kappa_{AA} C_{A1})\right] \tag{6}$$

Eq. (6) can be approximated by

$$J_A = \frac{D_{A0}}{\delta}(C_{A2} - C_{A1})\left(1 + \frac{\kappa_{AA}}{2}(C_{A2} + C_{A1})\right) \tag{7}$$

At the limit of $\kappa_{AA} \to 0$, i.e., no plasticization action, Eq. (7) reduces to

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$$J_A = \frac{D_{A0} C_{A2}}{\delta}\left(1 - \frac{C_{A1}}{C_{A2}}\right) \tag{8}$$

When $p_l \rightarrow 0$, Eq. (7) reduces to

$$J_{A0} = \frac{D_{A0}}{\delta} C_{A2}\left(1 + \frac{\kappa_{AA}}{2} C_{A2}\right)$$

$$= \frac{D_{A0}}{\delta} m_A C_T x_A \left(1 + \frac{\kappa_{AA}}{2} m_A C_T x_A\right) \tag{9}$$

The permeation flux here varies quadratically with the weight fraction of water in the feed solution.

At the limit of $\kappa_{AA} \rightarrow 0$, Eq. (9) reduces to

$$J_{A0} = \frac{D_{A0}}{\delta} C_{A2} = \frac{D_{A0}}{\delta} m_A C_T x_A \tag{10}$$

Then, the permeation flux of water varies linearly with its weight fraction in the feed solution. The above equation can clearly be derived from Eq. (1) with both κ_{AA} and κ_{BA} equal to zero.

The diffusion flux of component B is given as

$$J_B = -D_{BO} \exp(\kappa_{BA} C_A) \frac{dC_B}{dx}$$

$$= -D_{B0}\{\exp(\kappa_{AA} C_A)\}^{\kappa_{BA}/\kappa_{AA}} \frac{dC_B}{dx} \tag{11}$$

From Eqs. (5) and (6), one gets the relationship between C_A and x:

$$\frac{x}{\delta} = \frac{\exp(\kappa_{AA} C_{A2}) - \exp(\kappa_{AA} C_A)}{\exp(\kappa_{AA} C_{A2}) - \exp(\kappa_{AA} C_{A1})} \tag{12}$$

Combination of Eq. (12) with Eq. (11) yields

$$J_B = -D_{B0}[\exp(\kappa_{AA} C_{A2} - \frac{x}{\delta}\{\exp(\kappa_{AA} C_{A2})$$

$$-\exp(\kappa_{AA} C_{A1})\}]^{\kappa_{BA}/\kappa_{AA}} \frac{dC_B}{dx} \tag{13}$$

By integration of the above equation with J_B constant. one gets

$$J_B = $$

$$\frac{(\kappa_{AA} - \kappa_{BA})\{\exp(\kappa_{AA} C_{A2}) - \exp(\kappa_{AA} C_{A1})\} D_{B0}(C_{B2} - C_{B1})}{\kappa_{AA}\delta[\exp\{(\kappa_{AA} - \kappa_{BA})C_{A2}\} - \exp\{(\kappa_{AA} - \kappa_{BA})C_{A1}\}]}$$

$$\text{for } \kappa_{BA} \neq \kappa_{AA} \tag{14}$$

and

$$J_B = \frac{\{\exp(\kappa_{AA} C_{A2}) - \exp(\kappa_{AA} C_{A1})\} D_{B0}(C_{B2} - C_{B1})}{\kappa_{AA}\delta(C_{A2} - C_{A1})}$$

$$\text{for } \kappa_{BA} = \kappa_{AA} \tag{15}$$

Eq. (14) can be approximated by

$$J_B = \frac{D_{B0}}{\delta}(C_{B2} - C_{B1}) \frac{1 + \kappa_{AA}(C_{A2} + C_{A1})}{1 + (\kappa_{AA} - \kappa_{BA})(C_{A2} - C_{A1})} \tag{16}$$

EXPERIMENTAL

1. Membrane Preparation

The polymer membranes were prepared by using chitosan (deacetilation 88%) from Tokyo Chemical Co. Ltd., Japan. First, Chitosan was dried at 60°C for 48 hours. Afterwards, 3 g of chitosan was added to 200 ml of 2 wt% aqueous acetic acid solution at room temperature under stirring for 24 hours. A chitosan solution was filtered with glass filter to remove dirts and undissolved chitosan, and then dried at room temperature to evaporate the solvent up to a 10 wt% polymer solution.

The polymer solution was cast on a glass plate and dried in an oven at 60°C for 12 hours. The casting solution and the plate were immersed into a 1 N aqueous NaOH solution, and dried again at 60°C for more than 12 hours to remove the residual solvent [Lee et al., 1991]. The density of dried membrane was determined to be 1.4227 g/cm^3 by a density gradient column method [Lee et al., 1991]. The average thickness of membrane used in this work was 0.05 mm.

2. Sorption Experiment

The chitosan membranes dried in a vacuum oven were put into a sealed sample bottle along with the feed solution. Then the sample bottle was maintained at 40°C in the water bath. After 24 hours, the sorbed amount was obtained from measurement of the weight of membrane removing the surface water every uniform interval until the value of measurement is kept constant. The equilibrium concentration of sorption was obtained by using the vacuum desorption equipment and gas chromatography.

3. Permeation Experiment

The water flux was measured at a constant cell temperature of 40°C and various downstream pressures ranging from 0.5 to 20 torr. Also, in oder to investigate the effect of feed temperature on the membrane performance, the total flux was measured at a constant downstream pressure of 0.5 torr and a water weight fraction of 0.1002. But the feed temperature was varied from 25°C to 50°C. Detailed description of the apparatus for sorption and permeation experiments could be found elsewhere [Bae et al., 1994a].

RESULTS AND DISCUSSION

Fig. 1 shows the relations between the sorbed amounts for pure water and water-ethanol mixtures, and the weight fraction of water. Also the relation between the permeation flux of water at the limit of $p_l \rightarrow 0$ (J_{A0}) and the weight fraction of water in the upstream solution was represented in the same figure. It is apparent from this figure that both the total sorbed concentration (C_T) and the concentration of sorbed water (C_A) obey linear relations with the weight fraction of feed water (x_A). Thus this system can be regarded as an ideal system in the same manner as Raoult's law in the vapor-liquid equilibrium. Mathematically, the equilibrium concentrations of water and ethanol in the membrane can be representd as

$$C_A = 2.12 \times 10^2 x_A\,[\text{kg/m}^3] \tag{17}$$

$$C_B = 1.16 \times 10^2 (1 - x_A)[\text{kg/m}^3] \tag{18}$$

On the other hand, the permeation flux for water at the limit of zero downstream pressure does not increase linearly with the weight fraction of water in the upstream solution (x_A), but seems to increase quadratically with increasing x_A. This trend

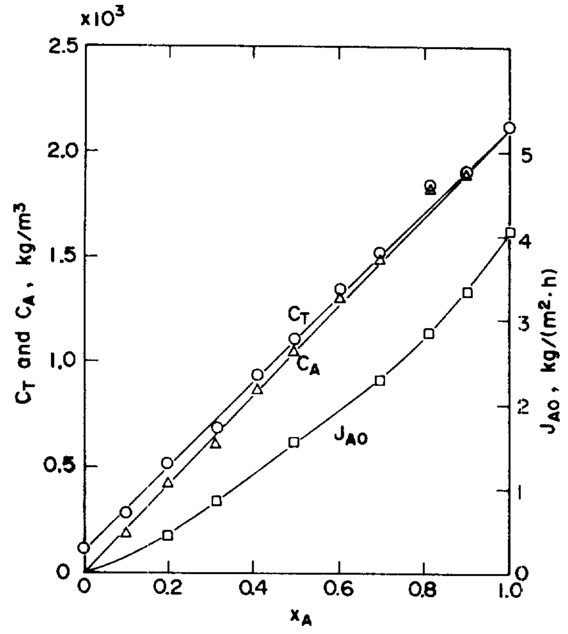

Fig. 1. Equilibrium concentration of ethanol-water and water and permeation flux at the limit of zero downstream total pressure as a function of weight fraction of water in the feed stream at 40°C.

conforms to Eq. (9). Plasticization action of sorbed water to the polymer might exert the diffusion process rather than the sorption process.

The experimental evidence that the plasticization effect of sorbed penetrant exerts the diffusion process rather than the sorption process, has been observed in the permeation for carbon dioxide in certain glassy polymer membranes [Bae et al., 1993; Bae et al., 1994b].

The effect of downstream pressure (p_l) on the permeation flux of water (J_A) was shown in Fig. 2. It was observed from this figure that J_A decreased linearly with increasing p_l. This experimental evidence can be understood as follows: p_{A1} is much larger than p_{B1} and nearly equal to p_l, and besides $C_{A2}>>C_{A1}$. Then Eq. (7) can be simplified into

$$J_A = \frac{D_{A0}}{\delta}\left(C_{A2} + \frac{K_{AA}}{2}C_{A2}^2 - C_{A1}\right) \qquad (19)$$

From Eq. (19), J_A decreases linearly with C_{A1} which is approximately proportional to p_l.

The slopes of the straight lines for x_A=0.313, 0.496 and 0.696 in Fig. 2 are constant, and such an experimental evidence means that the Henry's law constant for water (H_A) is constant in this range of x_A. The slope of the straight line for pure water (x_A=1.0) is larger than the former slopes, and the value of Henry's law constant for pure water is smaller than a constant value for x_A=0.313, 0.496 and 0.696.

The temperature dependence of the total flux (at x_A=0.1002) is illustrated in Fig. 3. It is considered that the structure of membrane is not changed for the temperature range used in this work because the permeation flux fits well to Arrhenius equation. The apparent activation energy is calculated to be 30.7 kJ/mol when weight fraction of water (x_A) is 0.1002.

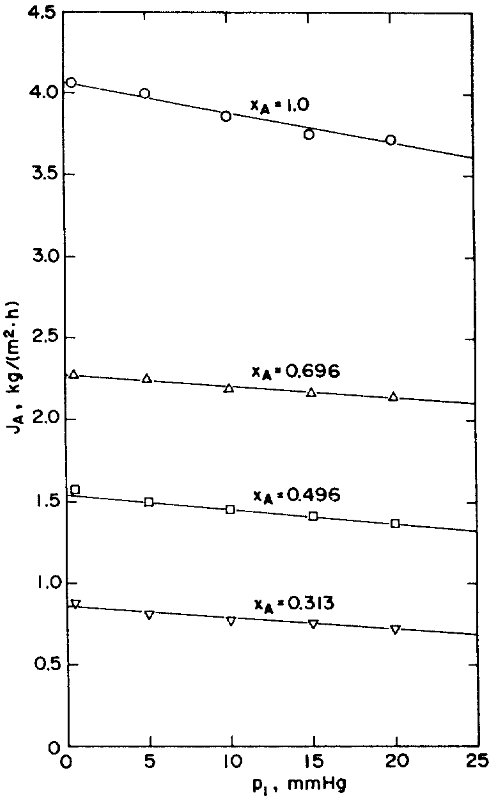

Fig. 2. Dependence of permeation flux for water on the downstream total pressure at various weight fractions of water in the feed stream at 40°C.

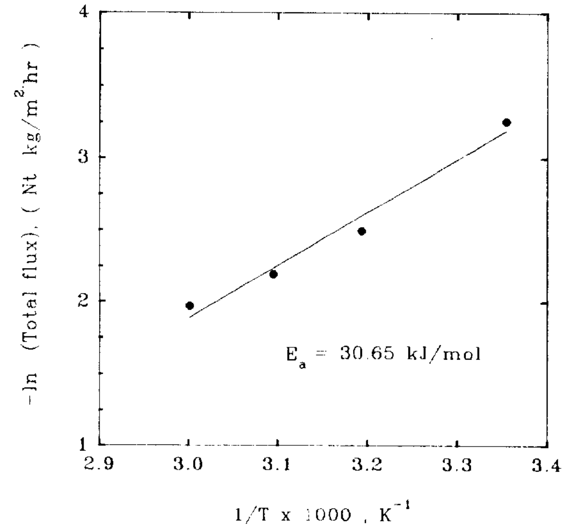

Fig. 3. Arrhenius plot for permeation flux at x_A=0.1002.

The pervaporation for aqueous ethanol solutions in a chitosan membrane to be discussed here can be regarded as a system with high ideality in the sorption process, whereas that in a cellulose triacetate (CTA) membrane is a system with high non-ideality [Bae et al., 1994b]

That is, the mole fraction of water in the feed solution had a great influence on the sorbed amount and the permeation flux [Bae et al., 1994b]. The relation of the total permeation flux at the limit of $p_l \rightarrow 0$ to the total sorbed amount in the membrane

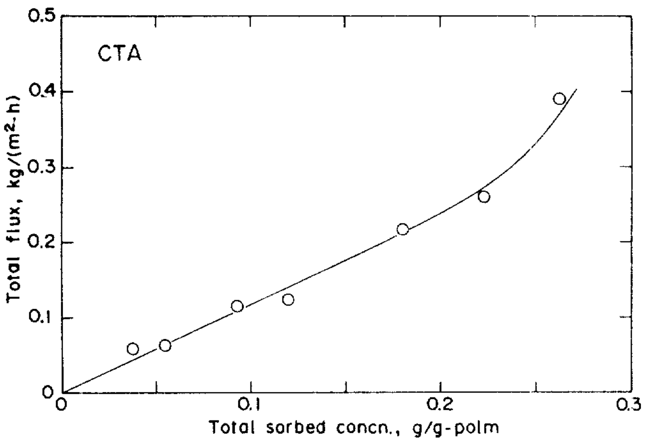

Fig. 4. Relationship between total permeation flux at the limit of zero downstream pressure and total sorbed concentration for ethanol-water mixture at 40°C.

instead of water weight fraction in the feed solution, is shown in Fig. 4. A straight line passing through the origin can be drawn up to a total sorbed concentration of 0.2 g/g-polymer, and above 0.2 g/g-polymer the plot considerably deviates from the straight line. Such an upward deviation may be due to the effect of the 2nd term in the bracket at the right-hand side of Eq. (9).

CONCLUSION

The process of pervaporation in which two components diffuse in a nonporous polymer membrane was formulated on the basis of a phenomenological model, when one of the penetrants can exert a plasticization effect on the membrane material. Exact and approximate solutions for the flux of component A were derived, when only component A exerted the plasticization action to the polymer membrane. The pervaporation behavior for aqueous ethanol solution in chitosan membrane was investigated by measurements of sorption equilibria and permeation fluxes, and compared with the proposed model. The total sorbed concentration and the concentration of sorbed water were found to be linear with the weight fraction of water (x_A) in the feed solution. But the permeation flux of water in chitosan membrane is influenced by the plasticization action of sorbed water to the polymer membrane. The plasticization action of sorbed water might exert the diffusion process rather than the sorption process.

NOMENCLATURE

C : concentration of penetrant in membrane $[kg/m^3]$
D : diffusivity in membrane $[m^2/s]$
H : Henry's law constant $[Pa \cdot m^3/kg]$
J : permeation flux $[kg/(m^2 \cdot h)$ or $kg/(m^2 \cdot s)]$
m : partition coefficient between liquid and membrane phases
p : total pressure [Pa or mmHg]
p_I : partial pressure of component I (I = A, B) [Pa]
x : position coordinate in the net flux direction [m]
x_I : weight fraction of component I (I = A, B)
δ : thickness of membrane [m]
κ : concentration-dependent parameter appearing in Eqs. (1) and (2) $[m^3/kg]$

Subscripts

A : component A or water
B : component B or ethanol
T : total
0 : zero concentration state or zero downstream pressure
1 : downstream surface
2 : upstream surface

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