A Qualitative Investigation on the Importance of Boundary Layer in Pervaporation Separation of an Aqueous Organic Reaction

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ABSTRACT: The importance of boundary layer was investigated for the hydrolysis of ethyl acetate using a dense standard poly(vinyl alcohol) (PVA) membrane. A resistance in a series model approach was used to study the effect of a boundary layer for the permeation of aqueous organic mixtures involved in the study. The initial feed mixture consisted of 10% water (H₂O), 40% ethyl acetate (EA), 50% acetic acid (AA), and 0% ethanol (E) (all weight percentage basis). The experiments were conducted at 65°C. The amount of all species in the feed reservoir was found to decrease with time. Selectivity calculations based on a resistance in the series model approach indicates that the boundary layer contributes to selective permeation of aqueous organic compounds. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2361–2369, 1998

Key words: boundary layer; aqueous organic separations; pervaporation; PVA membrane

INTRODUCTION

The pervaporation process has been employed for a variety of separation tasks.¹⁻⁹ Baker¹⁰ has delineated the merits of a pervaporation process for organic contaminant removal.

The mass transport from the liquid feed to the vapor permeate can be described by a resistancein-series model.^{11,12} This model involves the following 4 steps.

- 1. Transport of the penetrants from the bulk of the feed to the feed–membrane interface.
- 2. Partition of the penetrants between the liquid feed and the membrane (boundary layer).
- 3. Transport of penetrants through the membrane.

4. Desorption of penetrants to the vapor phase at the permeate side of the membrane.

Pervaporation studies generally indicate that steps 2 and 3, above, are 2 important process contributing to the overall performance of the pervaporation process.^{11–14}

Few citations that indicate the presence of a liquid boundary layer, which inherently exists in mass transfer operations, are the early investigations carried out by Hwang and coworkers,^{11–13} who studied the transport of dissolved gases, such as oxygen and carbon dioxide, through silicone rubber membranes. It was observed in their study that solute transport across the membrane was seriously limited by boundary layer mass transfer resistance. A similar effect was observed by Refojo and Leong¹⁴ for dissolved oxygen transport through hydrogel contact lenses. In pervaporation, boundary layer resistance to solute transport was reported by Psaume et al.¹⁵ for trichlo-

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Figure 1 Profile of an organic compound during pervaporation.

roethylene removal from aqueous solutions. It was observed in this study that solute transfer through the membrane was primarily determined by the hydrodynamic conditions on the feed side, and the membrane resistance was relatively unimportant. A recent study by Colman et al.¹⁶ showed that boundary layer mass transfer resistance can be a significantly limiting factor in the dehydration of isopropanol–water by pervaporation.

Transport through the membrane, which is a major resistance offered in mass transfer, is based on the solution diffusion mechanism. Flux in this case can be described by Fick's law.¹⁴

The objectives of this investigation are to investigate the selectivities and flux of water, ethyl acetate and acetic acid (reactants), and ethanol (product) in a hydrolysis reaction using a simple resistance-in-series model approach for a standard poly(vinyl alcohol) (PVA) membrane. PVA

Table I

selectivity to different substances is determined as a function of temperature and time. Though the resistance model approach is not a mechanistic approach to membrane separation, it has practical application to membrane development because it correlates membrane selectivity and the resistance components lying in the path of mass transport through the membrane and offers a means of determining these resistances qualitatively.

THEORETICAL

The yield of each species was calculated on the basis of the number of moles of each component in the feed and permeate, as follows:

$$Yield = \frac{Moles of a particular species}{total moles of the same species} (1)$$
$$(feed + permeate)$$

The permeation flux of a component represents the amount of component passing per hour and square meter of membrane area. It is given by

$$J_i = W_i J_T \tag{2}$$

where J_i , W_i , and J_T represent the permeation flux of individual species, weight fraction of the i^{th} component, and the total flux.

Mass transport of a permeating component in a membrane pervaporation can be written as¹⁷

$$[MT] = K.A.\frac{\gamma p_s X - pY}{l}$$
(3)

where [MT] is the mass transport; γ is the activity coefficient; *A* is the area and *l* is the thickness

	\mathcal{D}^{o}	Do	P_n^o	P_n^o	
Temperature			Acetic	Ethyl	
(°K)	H_2O	Ethanol	Acid	Acetate	P_n
					0.418 imes105
338	0.02499	0.0584	0.01533	0.0673	338

Note: P_n is the partial pressure above solution (Pascal) and P_n^o is the vapor pressure of pure component (Pascal) (where *n* represents water, ethanol, acetic acid, and ethyl acetate).



Figure 2 Schematic presentation of the permeation cell: (1) metal ring; (2) gasket; (3) membrane; (4) porous metal filter; (5) support disc; (6) cock.

of the membrane; K is the effective permeability coefficient that accounts for nonideal behavior of the feed mixture; X and Y are the mole fractions of the permeating species in the feed and the permeate, respectively; and p and p_s refer to the permeate pressure and the saturated vapor pressure, respectively.

Defining the membrane resistance (*R*) and the driving force (Δu) for the permeation as

$$R = l/KA \tag{4}$$

$$\Delta u = \gamma p_s X - pY \tag{5}$$

Equation (3) becomes

$$[MT] = \Delta u/R \tag{6}$$

which is similar to Ohm's law in an electric circuit.

It is a well-known fact that a liquid boundary layer causes a decrease in pervaporation selectivity.^{15–17} Consider the permeation through a dense PVA membrane shown in Figure 1.

The overall permeation resistance R_t can be given as

$$R_{t} = R_{1} + R_{2}$$

where R_1 is the resistance of membrane layer and R_2 is the resistance of the liquid boundary layer. R_1 can be given as



Figure 3 Plot indicating the variation of the yield of each component at 65° C versus time.



Mole fraction (water)

Figure 4 Permeation flux at 65°C versus the mole fraction of feed water.

$$R_1 = \frac{l}{p_{(c)}} \tag{7}$$

where l is the membrane thickness and $p_{(c)}$ is the permeability of the membrane to the particular component.

$$R_2 = \frac{1}{k_L} \tag{8}$$

 k_L represents the individual liquid layer resistance. The basic equations to determine the effect of liquid boundary layer in the pervaporation process can be given as¹⁸

$$J = k_{a,v} \cdot \phi^b \tag{9}$$

 $k_{o.c.}$, the overall mass transfer coefficient, can be calculated from eq. (9). In eq. (9), J represents the individual permeate flux in pervaporation experiments and ϕ^b represents the concentration in the bulk feed.

The total resistance R_t can be given as

$$R_t = \frac{l}{p_c} + \frac{1}{k_L} = \frac{1}{k_{o.v}}$$
(10)

 k_L , the individual liquid layer resistance, is obtained from eq. (10).

The separation factor can be defined as

$$\alpha_{\rm H_2O/(o.c)} = \frac{Y_{\rm H_2O}/Y_{(o.c)}}{X_{\rm H_2O}/X_{(o.c)}}$$
(11)



Figure 5 Permeation flux at 65°C versus time.

where X and Y are the species weight fractions in feed and permeate, respectively. The subscripts H_2O and (o.c) represents water and organic compound.

$$\alpha_{\rm H_2O/(o,c)} = \frac{[MT]_{\rm H_2O}/[MT]_{(o,c)}}{X_{\rm H_2O}/X_{(o,c)}}$$
(12)

when the permeate pressure *p* is sufficiently low, $\gamma p_s X \gg pY$, for both permeating species; then eq. (12) can be simplified to the following form:

$$\alpha_{\rm H_2O/(o.c)} = \frac{\gamma_{\rm H_2O}(P_s)_{\rm H_2O}(R_t)_{(o.c)}}{\gamma_{(o.c)}(P_s)_{(o.c)}(R_t)_{\rm H_2O}}$$
(13)

Neglecting the boundary layer effects, eq. (13) can be modified to obtain the intrinsic selectivity as

$$\alpha_{\rm int(H_2O/o.c)} = \frac{\gamma_{\rm H_2O}(p_s)_{\rm H_2O}}{\gamma_{\rm (o.c)}(p_s)_{\rm (o.c)}} * \frac{\left(\frac{l}{p}\right)_{\rm H_2O}}{\left(\frac{l}{p}\right)_{\rm (o.c)}}$$
(14)

where α_{int} represents the intrinsic selectivity of the membrane

The activity coefficient γ , which is a correction factor compensating for nonideal behavior, was determined using the following equation¹⁹:

$$P_n = \gamma_n x_n P_n^o \tag{15}$$

where *n* represents components like water, ethanol, acetic acid, and ethyl acetate, and P_n , γ_n , x_n , and P_n^o denote the partial pressure above solution, activity coefficient of a typical component, mole fraction of the component, and vapor pressure of the pure component. The partial pressure of the solution and vapor pressure of pure components are indicated in Table I. The γ , estimated from eq. (15), was used in eqs. (13) and (14).

EXPERIMENTAL

The pervaporation experiments were carried out in the apparatus shown in Figure 2. Separation



Figure 6 Plot indicating selectivity at 65°C.

was carried out using a standard PVA membrane supplied by G.F.T. Germany. The membrane was located in the permeation cell over a porous glass support. The membrane thickness and effective surface area are 2 μ m and 0.5 m², respectively.

The feed solution (2 L) was kept in a tank that acted as the feed reservoir. Pervaporation experiments were conducted for a feed composition, which initially consisted of water 10% (H₂O), 40%ethyl acetate (EA), and 50% acetic acid (AA), Ethanol (E) was a side product of the hydrolysis reaction. The feed temperature could be varied between -20 to 150° C, by circulation through a heat exchanger and a thermostated water bath [see Fig. 2(a)]. A constant downstream pressure (6.5 \pm 0.5 torr) was maintained with a vacuum pump. The experiments were conducted at 65°C. The measurement error in the system temperature was limited to ± 0.5 °C. The vaporized permeate was condensed by operating the cold trap at a temperature of -20° C. Further details for the experimental system can be found in previous investigations by the author.^{20–22}

At start of each experimental run, the system was operated for 1 h with no condensation and sample collection. This was necessary to ensure steady-state operating conditions. The pervaporated vapor was withdrawn every 1 h, weighed, and analyzed using a gas chromatograph equipped with a Porapak Q column heated to 160°C. A thermal conductivity detector and helium carrier gas were used in the gas chromatograph.

RESULTS AND DISCUSSION

Pervaporation data were collected for a mixture of water, ethyl acetate, and acetic acid. The following includes discussion of collected data and calculated system variables, which were defined in the theory section. The discussions were based on variations in system parameters and water feed concentration at 65°C.

The yield of different species in the permeate was calculated as per eq. (1). Figure 3 shows the yield of different components obtained at 65°C as a function of operation time. Figure 3 indicates that the PVA membrane is highly water permselective. The maximum amount of water permeated is around 97%. The water concentration is found to decrease with time. This could be due to its high initial concentration. The membrane is also found to permeate ethanol. A maximum yield of around 78% was obtained. The concentration for ethanol was found to decrease as a function of time. The yield of acetic acid was found to gradually increase from 44% to a maximum value of 57% at the tenth hour. The initial permeation value for ethyl acetate was around 20%. It increases gradually to 38% over a period of 12 h. The results for acetic acid and ethyl acetate indicate that the membrane is less selective to both these compounds. From Figure 3, it can be concluded that permselectivity of PVA membrane to a hydrolysis mixture consisting of water, acetic acid, ethanol, and ethyl acetate follows the following order: water > ethanol > acetic acid > ethyl acetate.

Figure 4 shows the variations in the species permeation flux as a function of the mole fraction of feed water at 65°C. The figure indicates that PVA membranes have a higher affinity for water compared to ethanol, acetic acid, and ethyl acetate. For water, the highest flux obtained is around 0.0467 kg m⁻² h⁻¹. At 65°C, the acetic acid and ethyl acetate had a maximum flux of 3.15×10^{-2} and 1.6×10^{-2} kg m⁻² h⁻¹. The low values of ethanol are because of the small amounts of ethanol, which exist in the feed mix-



Figure 7 Plot indicating intrinsic selectivity at 65°C versus time.

ture. As a result, the total amount of ethanol permeating through the membrane over the same mole fraction of water is much lower than the 2 species.

Figure 5 shows variations in the permeation flux of water, ethanol, acetic acid, and ethyl acetate for an operating temperature of 65°C as a function of operating time. This figure indicates that the PVA membrane is highly water permselective. The initial permeation flux of water is around 0.0467 kg m⁻² h⁻¹ at 65°C. The low flux values of ethanol, as seen in Figure 5, could be due to its small amount in the feed mixture. As seen in Figure 5, the permeation flux of acetic acid and ethyl acetate was the highest in the initial 2 h of the reaction. The flux for acetic acid at 65°C was 3.15×10^{-2} kg m⁻² h⁻¹; while for ethyl acetate, it was 1.6×10^{-2} kg m⁻² h⁻¹.

In the resistance-in-series model considered above, the first step in the pervaporation process is mass transfer from the bulk of the feed to the feed-membrane interface. The penetrants are convectively transported from the bulk of the feed towards the membrane surface; but due to selectivity, the net uptake in the membrane of the slower penetrant is not as high as the net uptake of the faster penetrant. This, in combination with the depleting feed flow velocity towards the membrane surface, in relation to the main stream velocity, will result in a region close to the membrane, the boundary layer, where diffusive mass transfer is important. The selectivity and intrinsic selectivity of the PVA membrane was estimated using eqs. (13) and (14). Figure 6 indicates a gradual increase in selectivity values for water-ethanol with time. Ethanol is obtained as a side product on acid hydrolysis of ethyl acetate. The maximum selectivity value obtained for water-ethanol is 13 at the tenth hour. The selectivity values decreased to 3 over a period of 15 h. The low selectivity values of ethanol could be due to its

low concentration. The maximum selectivity values for ethyl acetate and acetic acid was around 72 and 27. The selectivity values indicate that a slower penetrant, like ethyl acetate and acetic acid, are rejected by the membrane in comparison to a faster penetrant like ethanol. The molecules, like acetic acid and ethyl acetate, could also exist as dimers, causing a decrease in the penetration rate. Equation (14) indicates that intrinsic selectivity values are independent of resistance offered by the boundary layer. Figure 7 indicates a plot of intrinsic selectivity at 65°C as a function of time. The plot shows the competition between different molecules to permeate through the PVA membrane in absence of a boundary layer. Intrinsic selectivity values of 12, 11, and 2.5 were obtained for water-ethyl acetate, water-ethanol, and water-acetic acid. These values are found to remain constant for the first 6 h. These values steeply rise to 33, 28, and 7 in a period of 5 h, which could qualitatively be attributed to depletion of the boundary layer. The relatively low selectivity values of Figure 7 compared to Figure 6 indicate the qualitative importance of a boundary layer in obtaining improved selectivity.

CONCLUSION

PVA membrane predominantly permeates water from aqueous organic mixtures in a hydrolysis reaction. This is dependent on the affinity of PVA to water in the mixture. The high perm-selectivity for water is mainly due to its small molecular size.

The yield of each species permeated in the hydrolysis reaction followed the order of water > ethanol > acetic acid > ethyl acetate. The yield of water and ethanol is found to decrease with time, while that of acetic acid and ethyl acetate increases with time.

The permeation flux of all the species is found to decrease with time at 65°C; the trend observed was water > acetic acid > ethyl acetate > ethanol. Concentration of ethanol was found to be the least. This could possibly be due to its low concentration.

Estimation of selectivity and intrinsic selectivity based on a resistance in the series model approach predicts that the boundary layer contributes to selective permeation of organic species in hydrolysis of ethyl acetate. The authors thank the Research Department of Kuwait University for providing funds from Project EC078 to carry out this work.

NOMENCLATURE

- K = permeability coefficient (kg m kg⁻¹ s m² kPa m s)
- A = area of membrane (m²)
- p_s = saturated vapor pressure (Pa)
- X = permeating species mole fraction in feed
- p = permeate pressure (Pa)
- Y = permeating species mole fraction in permeate
- l =thickness of membrane (m)
- R_t = total membrane resistance
- Δu = driving force for permeation
- $p_{(c)} =$ permeability of membrane to a particular component
 - J = permeation flux of individual components (kg m⁻² h⁻¹)
- J_T = total flux (kg m⁻² h⁻¹)
- $k_{o.v}$ = overall mass transfer coefficient
- R_1 = resistance offered by membrane layer
- R_2 = resistance offered by boundary layer
- k_1 = individual liquid layer resistance
- P_n = partial pressure above solution (Pa)
- x_n = mole fraction of component
- $P_n^o =$ vapor pressure of pure component (Pa)
- W_i = weight fraction of *i*th component γ = activity coefficient
- $\alpha_{H_2O/o.c}$ = selectivity of water to organic component
- $\alpha_{int_{(H_2O/o.c)}} = \underset{component}{intrinsic selectivity of water to organic}$
 - ϕ^b = bulk feed concentration (kg/m³)

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