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Modeling of Pervaporation with Latex Membranes

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ABSTRACT

Latex membranes have shown potential to be a new type of pervaporation separation membrane. Three types of latex membranes were prepared in our laboratory by direct casting of polymer latexes. These latex membranes were selective toward water during pervaporation with ethanol–water mixtures. The free-volume approach was employed to characterize the pervaporation of these latex membranes. It is shown by this experiment that the Yeom–Huang model, which is based on the free-volume theory and the thermodynamics, can be used to model the pervaporation process of the latex membranes which give reasonable predictions on the permeability.

Key Words. Latex membrane; Pervaporation; Free-volume theory; Yeom–Huang model

INTRODUCTION

It is always desirable if the separation properties of a given pervaporation system can be predicted or at least be estimated based on some simple experimental results or data available in the literature. Therefore, modeling of pervaporation separation has been extensively studied in the past.

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Lee, Mulder, and Smolders (1–3) used a solution-diffusion model in which the diffusion coefficient is either assumed to be concentration independent or has an exponential relationship with concentration, but the mutual interactions between components and between the components and the membrane were not considered. Greenlaw et al. (4) adopted a linear relationship between concentration and permeability by using the diffusion coefficient of an ideal liquid mixture containing heptane and hexane. A "six coefficient exponential model" was proposed by Brun (5). By employing Fujita's free volume theory, Fels and Huang (6–8) developed a model to predict the permeation rate during pervaporation (9). A later modification made by Rhim and Huang (10) introduced the Flory–Huggins interaction parameters in order to consider mutual interactions of the individual components and the membrane which may be significant in nonideal solutions. Recently, Yeom and Huang (11) developed a mathematical methodology to model the pervaporation process, taking into account the coupling fluxes. This model was a further modification of the Fels–Huang and Rhim–Huang models. The solubility data of the individual components measured from equilibrium sorption experiments were used as the boundary conditions at the upstream side of the membrane. The Yeom–Huang model was shown to give an accurate prediction on the pervaporation properties of crosslinked poly(vinyl alcohol) membranes (11).

Modeling a latex membrane system is more difficult than modeling solvent cast membranes since the latex membrane is a heterogeneous system (12). So far there has been no study in modeling the pervaporation of latex membrane systems. Although a comprehensive transport mechanism was proposed for such membrane systems (13), prediction of the pervaporation property based on those equations is not practical because the volume fractions, diffusion coefficients, and the concentration profile of the polymer bulk and boundary region can not be individually measured or estimated. As an alternative, the latex membrane is treated as a homogeneous system and its structure details are neglected. Such an assumption makes it possible to model the latex membrane system in a way similar to solvent cast membranes (13). The free volume approach, which was used by Yeom and Huang (11), is therefore adopted to characterize the pervaporation of latex membrane system with ethanol–water mixtures.

CALCULATION METHOD

The Yeom–Huang model for the characterization of the pervaporation separation of solvent cast membranes was detailed in Reference 11. The following gives the basic calculation method as modified to apply to latex membrane systems.

The permeant transport through a latex membrane is described according to the solution-diffusion mechanism (13). The steady-state permeation of a single component can be related by Fick's first law with a concentration-dependent diffusion coefficient:

$$J_i = -D_i \frac{\partial c_i}{\partial x} \tag{1}$$

where D_i is identical to the overall diffusion coefficient when the latex membrane is assumed to be homogeneous. In order to simplify the calculation, the following assumptions are made:

1. Diffusion only occurs in the amorphous region of the membrane, and crystallites are impermeable to permeant.
2. The membrane is in an isothermal condition due to its thinness.
3. During pervaporation, the sorption is in equilibrium.
4. The concentration of the permeant is zero at the permeate side due to the low pressure.
5. The volume fraction of a component in a membrane is equal to the volume fraction at equilibrium sorption.

According to Fujita's free volume theory (9, 14), D_i in Eq. (1) is related to the thermodynamic diffusion coefficient $(D_T)_i$:

$$D_i = (D_T)_i \frac{\partial \ln a_i}{\partial \ln v_i} \tag{2}$$

where a_i and v_i are the chemical activity and volume fraction of component i in the membrane, respectively. $(D_T)_i$ is expressed by

$$(D_T)_i = RTA_{di} \exp\left[\frac{-B_{di}}{f(v_i, T)(1 - \phi_c)}\right] \tag{3}$$

where A_{di} and B_{di} are the free volume parameters which are characteristic for a given polymer–penetrant pair, $f(v_i, T)$ is the free volume fraction of the membrane system at temperature T, and ϕ_c is the degree of crystallinity of the membrane. Since the latex membranes used are essentially amorphous (12), Eq. (3) reduces to

$$(D_T)_i = RTA_{di} \exp\left[\frac{-B_{di}}{f(v_i, T)}\right] \tag{4}$$

The free volume fraction $f(v_i, T)$ of a binary system is given by

$$f(v_i, T) = f(0, T) + \beta_i(T)v_i \tag{5}$$

where $f(0, T)$ is the free volume fraction of the polymer itself and $\beta_i(T)$ is a proportional constant relating the amount of free volume increased by the diffusion species i. When $v_i = 0$ in Eq. (5), the diffusion coefficient at zero concentration, D_{i0}, is given by

$$D_{i0} = RTA_{di} \exp\left[\frac{-B_{di}}{f(0, T)}\right] \tag{6}$$

The free volume fraction of a ternary system (binary mixture–membrane) is expressed as

$$f(v_i, T) = f(0, T) + \beta_1(T)v_1 + \beta_2(T)v_2 \tag{7}$$

Therefore, in a ternary system:

$$(D_T)_1 = RT(A_d)_1 \exp\left[\frac{-(B_d)_1}{f(0, T) + \beta_i(T)v_1 + \beta_2(T)V_2}\right] \tag{8}$$

where $(A_d)_1$ and $(B_d)_1$ are the free volume parameters of Component 1 in a ternary system.

It was shown that the free volume parameters of a ternary system are actually identical to those of a binary system (11). Thus Eq. (8) can be written as

$$(D_T)_1 = RTA_{d1} \exp\left[\frac{-B_{d1}}{f(0, T) + \beta_i(T)v_1 + \beta_2(T)V_2}\right] \tag{9}$$

In pure liquid permeation, $\beta_i(T)$ can be calculated with the definition (when $v_i = 1$ in Eq. 5):

$$f(1, T) = f(0, T) + \beta_i(T) \tag{10}$$

The free volume fraction $f(1, T)$ is given by (15):

$$f(1, T) = \frac{v_f - v_0}{v_f} \tag{11}$$

where v_f is the specific volume of the liquid at any temperature T, and v_0 is the specific volume of the liquid extrapolated to the temperature 0 K without phase change.

The free volume fraction of polymer at a temperature below its glass transition temperature was related by Robert and White (16) to the prerequisite for the motion of chain segments. In the Yeom–Huang model (11),

$f(0, T)$ is assumed to be proportional to temperature in the temperature range shortly below T_g with a slope of $0.025/2T_g$, which is an average value for extreme cases (increasing free volume at above 0 K and constant free volume at T_g):

$$f(0, T) = 0.025 - \frac{0.025(T_g - T)}{2T_g} \tag{12}$$

The partial differential term in Eq. (2) of a binary system is given by the Flory–Huggins thermodynamics (17):

$$\begin{aligned} \frac{\partial \ln a_i}{\partial \ln v_i} &= 1 - \left(1 - \frac{V_i}{V_p}\right) v_i - 2\chi_{ip} v_i v_p \\ &\simeq 1 - v_i - 2\chi_{ip} v_i (1 - v_i) \end{aligned} \tag{13}$$

where V is the molar volume, subscript p represent polymer, and χ_{ip} is the interaction parameter characterizing the interactions between penetrant and the polymer membrane, which is defined by

$$\frac{\Delta G_m}{RT} = n_1 \ln \phi_1 + n_p \ln \phi_p + \chi_{1p} n_1 \phi_p \tag{14}$$

where ϕ is the volume fraction in equilibrium sorption. It has been shown (10):

$$\chi_{ip} = -\frac{\ln(1 - v_p) + v_p}{v_p^2} \tag{15}$$

To calculate the individual permeabilities in a ternary system, it is further assumed that both permeants diffuse independently, i.e., they are treated as two independent binary systems. For each binary system the permeation rate of component i given by Eq. (1) is expressed by

$$J_i = -\rho_i \int_0^{v_{i0}} (D_T)_i \frac{\partial \ln a_i}{\partial \ln v_i} \frac{dv_i}{dx} \tag{16}$$

For a ternary system, the sorption data of the same system can be used as the boundary conditions in conducting the integration. Integrating across the membrane thickness while using these boundary conditions, the permeability of component i (P_i) in the ternary system is given by

$$\begin{aligned} P_i = J_i L &= \int_0^L J_i \, dx \\ &= \rho_i \int_0^{v_{i0}} (1 - v_i)(1 - 2\chi_{ip}) v_i (D_T)_i \, dv_i \end{aligned} \tag{17}$$

where v_0 is the v_i value corresponding to ϕ_i at equilibrium sorption, and ρ is the density of the component.

To obtain the concentration profile of an individual component in the membrane, a relative distance in the membrane ($x_R = x/l$) is defined. Incorporating this definition with Eq. (17) gives Eq. (18):

$$x_R = \frac{x}{l} = \frac{\int_{v_i}^{v_{i0}} (1 - v_i)(1 - 2\chi_{ip} v_i) \exp\left[\frac{-B_{di}}{f(0, T) + \beta_i(T) v_i}\right] dv_i}{\int_0^{v_{i0}} (1 - v_i)(1 - 2\chi_{ip} v_i) \exp\left[\frac{-B_{di}}{f(0, T) + \beta_i(T) v_i}\right] dv_i} \tag{18}$$

Since x_R ranges between 0 and 1, the volume fraction of individual component v_i can be computed from Eq. (18). A numerical method is required to solve this equation.

EXPERIMENTAL

Membrane Preparation

Latexes of poly(acrylonitrile-*co*-butyl acrylate) [P(AN–BuA)], poly(methyl methacrylate-*co*-butyl acrylate) [P(MMA–BuA)], and poly(styrene-*co*-butyl acrylate) [P(ST–BuA)] were synthesized by emulsion polymerization as described in Reference 12. After being filtered with a nylon screen, the latexes were cast directly onto glass plates. The thickness of the film ranged from 80 to 120 μm.

After drying at ambient temperature in a filtration hood for 7 days, the membrane was carefully removed from the plate. Vacuum drying was then applied to the film at ambient temperature for 12 hours to remove any volatile residuals.

Sorption and Pervaporation

The equilibrium liquid uptakes were measured to obtain sorption data for the latex membranes. The pre-weighed, dry, and square-shaped membranes were immersed in bulk liquids of known ethanol concentration at 25°C for 2 weeks to allow the membranes to reach sorption equilibrium. After careful blotting off the surface liquid with tissue paper, the membranes were weighed as quickly as possible and then put into a dry flask which was connected to a liquid N_2 cold trap and a vacuum pump. The desorbed liquid was collected, weighed, and analyzed for composition with a Perkin-Elmer 8310 Gas Chromatograph to give the sorption amount and selectivity.

The pervaporation process is described in Reference 13. During pervaporation, the feed mixture was circulated by a circulation pump. The pressure at the permeate side was maintained below 3 mmHg. The permeant was collected in glass traps which were immersed in liquid nitrogen. Ethanol concentrations in the feed solutions tested were 15, 30, 50, 75, and 95 wt% ethanol. Pervaporation temperatures were 25, 35, 45, and 55°C.

RESULTS AND DISCUSSION

Equilibrium Sorption of Individual Component

The sorption of individual components in the latex membrane was determined in terms of its volume fractions. The sorption results are given in Tables 1 to 3. From these tables it can be seen that pure ethanol causes greater membrane swelling than does water. It is observed that for the P(AN–BuA) and P(MMA–BuA) membranes, the degree of membrane swelling by the binary mixture is maximum in the middle composition due to coupled sorption. For the P(ST–BuA) membrane the degree of swelling increases with increasing ethanol concentration due to the strong interaction between ethanol and the membrane. These sorption data were used as the boundary conditions at the upstream side of the membrane in simulating the individual permeabilities through the membrane.

Free Volume Parameters

To predict permeability, the free volume parameters should be obtained. For water, its free volume, $v_f - v_0$, in the temperature range of

TABLE 1
Equilibrium Sorption of P(AN–BuA) Latex Membrane with Ethanol–Water Mixture at 25°C

w_f[a]	ϕ_1[b]	ϕ_2	ϕ_p
0	0	0.206	0.794
0.15	0.022	0.253	0.725
0.30	0.108	0.236	0.656
0.50	0.181	0.174	0.645
0.75	0.219	0.077	0.704
0.95	0.217	0.026	0.757
1.0	0.226	0	0.774

[a] Ethanol weight fraction in feed.

[b] Volume fraction. Subscripts 1, 2, and p refer to ethanol, water, and polymer, respectively.

TABLE 2
Equilibrium Sorption of P(ST–BuA) Latex Membrane with Ethanol–Water Mixture at 25°C

w_f[a]	ϕ_1[b]	ϕ_2	ϕ_p
0	0	0.256	0.744
0.15	0.020	0.379	0.601
0.30	0.122	0.433	0.445
0.50	0.333	0.322	0.345
0.75	0.502	0.188	0.314
0.95	0.670	0.040	0.290
1.0	0.718	0	0.282

[a] Ethanol weight fraction in feed.

[b] Volume fraction. Subscripts 1, 2, and p refer to ethanol, water, and polymer, respectively.

0 to 150°C can be found in the literature (18). The calculation of v_f and extrapolation of the specific volume to 0 K were done by using a density function in the form of a Taylor expansion (11). The glass transition temperatures of P(AN–BuA), P(ST–BuA), and P(MMA–BuA) were 33.5, 42.5, and 27.3°C, respectively (12). Therefore the parameters $f(0, T)$, $f(i, T)$, and $\beta_i(T)$ can be obtained from Eqs. (10) to (12), and are listed in Table 4. The $\beta(T)$ values in this table indicate that the increase in the membrane free volume due to the presence of water is greater than that of ethanol, and thus contributes more to the plasticization of the membrane.

From Eqs. (8) and (9) it is seen that the larger the free volume fraction in the membrane, the larger the diffusion coefficient. Thus, any effects

TABLE 3
Equilibrium Sorption of P(MMA–BuA) Latex Membrane with Ethanol–Water Mixture at 25°C

w_f[a]	ϕ_1[b]	ϕ_2	ϕ_p
0	0	0.563	0.437
0.15	0.029	0.566	0.405
0.30	0.174	0.435	0.391
0.50	0.314	0.316	0.370
0.75	0.464	0.153	0.383
0.95	0.576	0.029	0.395
1.0	0.557	0	0.443

[a] Ethanol weight fraction in feed.

[b] Volume fraction. Subscripts 1, 2, and p refer to ethanol, water, and polymer, respectively.

that reduce the free volume of the membrane lead to a decrease in permeability. Therefore, when a latex membrane undergoes aging, the free volume reduces as a result of closer packing of the particles (13), and the permeability decreases.

The free volume parameters A_{di} and B_{di} are obtained from Eq. (3) by solving the equation with the thermodynamic diffusion coefficient of the pure component at different temperatures. The thermodynamic diffusion coefficient $(D_T)_i$ can be computed using Eq. (18) with the permeability of the binary system (pure component) at different temperatures. The free volume parameters are given in Table 4.

As shown by the free volume theory (9), B_{di} is an arbitrary parameter corresponding to the minimum size of the *jumping cell* or *hole* that is required for a given permeant molecule, *i*, to complete the diffusional displacement, and thus is related to the size of the permeant molecule. As expected, the B_{di} values for water in Table 4 are smaller than those of ethanol, because water has a smaller molecular size and requires a smaller cell to permit the diffusion jumping.

The binary interaction parameters characterizing the interaction between the individual component and the membrane at 25°C were calculated from Eq. (15) by using the equilibrium sorption data. They are given in Table 4. The interaction parameter is assumed to be concentration independent.

Diffusion Coefficient

The diffusion coefficients of the binary and ternary systems were calculated based on the corresponding equilibrium sorption data and the free volume parameters of the binary system with Eqs. (2) to (16). The results are presented in Table 5. As shown by this table, the diffusion of water in the membrane is faster than that of ethanol, apparently due to its smaller

TABLE 4
Free Volume Parameters at 25°C

	P(AN–BuA)		P(ST–BuA)		P(MMA–BuA)	
	Ethanol (1)	Water (2)	Ethanol (1)	Water (2)	Ethanol (1)	Water (2)
$f(0, T)$	0.02465	0.02465	0.02431	0.02431	0.02491	0.02491
$f(1, T)$	0.2310	0.2988	0.2310	0.2988	0.2310	0.2988
$\beta(T)$	0.20635	0.27415	0.20669	0.27449	0.20609	0.27389
$R(A_{di})$	8.85×10^{-13}	2.51×10^{-13}	2.17×10^{-15}	9.34×10^{-14}	9.1×10^{-15}	1.88×10^{-13}
B_{di}	0.2561	0.0211	0.3225	0.1517	0.5970	0.2212
χ_{ip}	1.191	1.246	0.620	0.519	0.724	0.720

TABLE 5
Diffusion Coefficient of Individual Components at 25°C

	w_f[a]	D_1 ($m^2 \cdot s^{-1}$)[b]	D_2 ($m^2 \cdot s^{-1}$)
P(AN–BuA)	0.0	0	5.4×10^{-11}
	0.15	1.81×10^{-11}	5.31×10^{-11}
	0.30	1.75×10^{-11}	4.00×10^{-11}
	0.50	1.18×10^{-11}	2.85×10^{-11}
	0.75	5.85×10^{-12}	2.25×10^{-11}
	0.95	3.5×10^{-12}	2.21×10^{-11}
	1.0	2.56×10^{-12}	0
P(ST–BuA)	0.0	0	5.53×10^{-9}
	0.15	5.37×10^{-11}	8.58×10^{-9}
	0.30	7.04×10^{-11}	5.21×10^{-9}
	0.50	4.24×10^{-11}	2.83×10^{-9}
	0.75	2.0×10^{-11}	1.16×10^{-9}
	0.95	5.6×10^{-12}	8.23×10^{-10}
	1.0	3.07×10^{-12}	0
P(MMA–BuA)	0.0	0	1.14×10^{-8}
	0.15	4.66×10^{-13}	1.16×10^{-8}
	0.30	2.33×10^{-13}	8.71×10^{-9}
	0.50	1.16×10^{-13}	5.91×10^{-9}
	0.75	2.53×10^{-14}	2.94×10^{-9}
	0.95	5.0×10^{-15}	1.24×10^{-9}
	1.0	2.5×10^{-15}	0

[a] Ethanol weight fraction in feed.

[b] Subscripts 1 and 2 refer to ethanol and water, respectively.

molecular size. It is also shown that the diffusion coefficient of the permeant in latex membranes is concentration dependent, which is also related to the free volume change in the membrane caused by the plasticization of the permeant.

For latex membranes the diffusion coefficient of ethanol decreases with increasing ethanol concentration in the feed, which is caused by the decrease in plasticization due to the decrease in water concentration. The diffusion coefficient of water, however, increases with its increasing concentration in the feed because of the high degree of self-plasticization of water.

Estimation of the Individual Permeability

The concentration profiles of individual components in the latex membranes can be calculated from Eq. (20) by a numerical solution of the equation. The concentration profiles at a feed composition of 0.5 weight fraction ethanol are given as typical examples and are shown in Figs. 1 to 3.

Knowing the diffusion coefficients, the concentration profile, and the equilibrium sorption data, which are used as the boundary conditions, the individual permeabilities of the components in a ternary system can be calculated using Eq. (17). The calculated permeabilities are listed in Tables 6 to 8 together with the experimental results. The ratio of the experimental to the calculated permeability is also given as an indication of the discrepancy. From the data in these tables it is seen that the estimates give reasonable agreement with the experimental results of the individual permeabilities, indicating that the free volume approach, which was developed originally to describe pervaporation with solvent cast membranes, can be adopted to characterize pervaporation with latex membranes.

Among the latex membranes, the predicted permeability through the P(ST–BuA) membrane is closest to the experimental ones. One possible reason for this observation is that the P(ST–BuA) latex membrane has a higher T_g than the others, for which the calculation of the free volume parameter is more accurate. For example, the free volume fraction of the membrane given by Eq. (12) is valid only for temperatures below its T_g. For the P(MMA–BuA) latex membrane, the accuracy is the lowest due

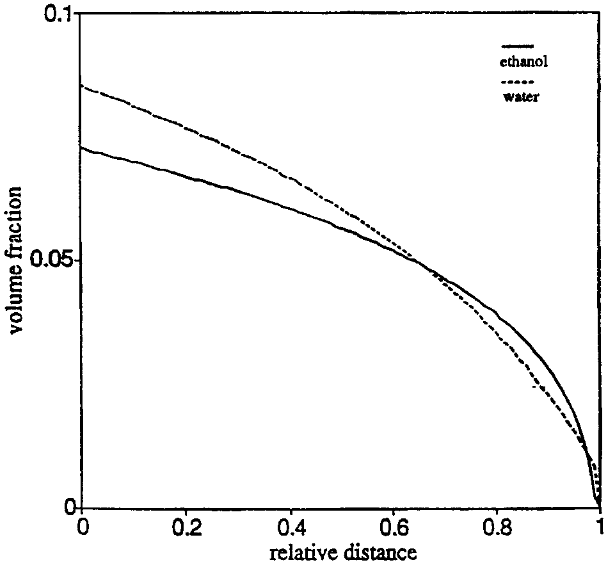

FIG. 1 Calculated concentration profile inside P(AN–BuA) latex membrane. 0.5 weight fraction ethanol in feed, feed temperature: 25°C.

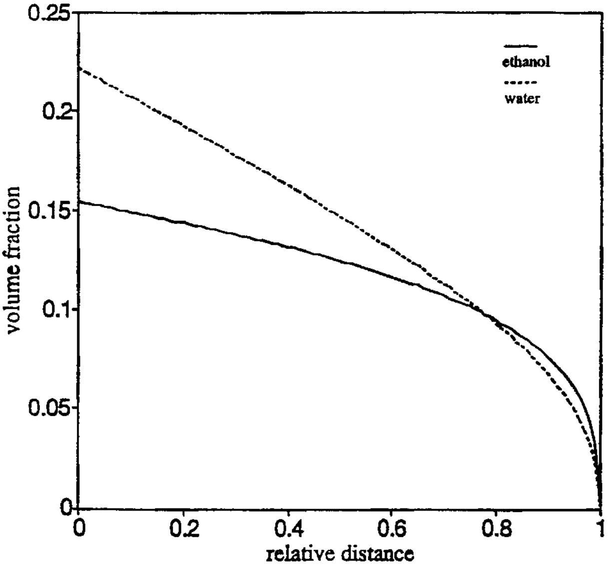

FIG. 2 Calculated concentration profile inside P(ST–BuA) latex membrane. 0.5 weight fraction ethanol in feed, feed temperature: 25°C.

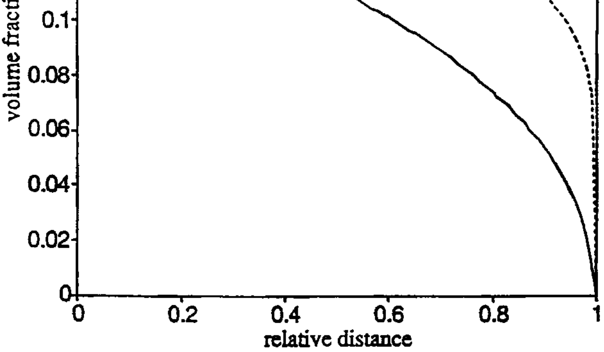

FIG. 3 Calculated concentration profile inside P(MMA–BuA) latex membrane. 0.5 weight fraction ethanol in feed, feed temperature: 25°C.

to its low T_g, and the membrane was actually in a rubbery state at the pervaporation temperature.

For ethanol permeability, the model gives the best estimation in the middle feed composition. But for water permeability, better prediction is found at a low ethanol concentration in the feed, in which case the membrane is less swollen.

The deviation between the calculated and experimental results shown in Tables 6 to 8 may come from different sources. Besides the experimental errors, deviation caused by the assumptions made in carrying out the computations may be significant. For example, it was assumed that sorption during pervaporation is in equilibrium, which is not true, particularly for the P(AN–BuA) latex membrane (13). Therefore, such an assumption causes greater deviation when used for the P(AN–BuA) membrane.

During calculation, the equilibrium sorption data were used as the boundary conditions. However, even for the diffusion-controlled pervaporation process, such as with the P(ST–BuA) latex membrane, a difference exists between the equilibrium sorption value and the concentration profile at the feed side of the membrane. This is because the chemical potential of a component in the feed is not equal to the chemical potential of this component just inside the membrane and because the interfacial resistance is not negligible.

The free volume approach, particularly the one recently developed in the Yeom–Huang model, was shown to provide excellent characterization for the pervaporation process of solvent cast membrane systems (11). Greater deviation is obvious when it is applied to latex membrane systems. One important source for this deviation is the assumption that the latex

TABLE 6

Experimental and Calculated Permeabilities of Individual Components through the P(AN–BuA) Latex Membrane at 25°C (permeability × 10^{-3} g/m·h)

	Ethanol		Water		Ratio	
w_f[a]	E[b]	C[c]	E	C	Ethanol	Water
0	0	0	2.12	3.87		0.6
0.15	0.061	0.019	2.76	5.96	3.2	0.5
0.30	0.20	0.055	3.40	5.33	3.7	0.6
0.50	0.35	1.41	5.51	3.19	0.3	1.7
0.75	0.96	1.25	5.46	0.67	0.8	8.2
0.95	1.18	0.73	3.11	0.58	1.6	5.4
1.0	3.76	0.61	0	0	6.2	

[a] Ethanol weight fraction in feed.

[b] Experimental value.

[c] Calculated value.

TABLE 7
Experimental and Calculated Permeabilities of Individual Components through the P(ST–BuA) Latex Membrane at 25°C (permeability × 10^{-3} g/m·h)

	Ethanol		Water		Ratio	
w_f[a]	E[b]	C[c]	E	C	Ethanol	Water
0	0	0	2.12	0.59		2.6
0.15	0.051	0.043	1.55	1.83	1.2	1.2
0.30	0.036	0.025	2.95	2.91	1.5	1.0
0.50	0.095	0.182	4.43	1.90	0.5	2.3
0.75	0.148	0.348	3.85	0.71	0.4	5.4
0.95	0.334	0.485	1.47	0.34	0.7	4.3
1.0	3.41	0.519	0	0	6.6	

[a] Ethanol weight fraction in feed.
[b] Experimental value.
[c] Calculated value.

membrane is a homogeneous system. Based on the latex membrane structure, the total free volume of a latex membrane should be the sum of the free volume in the polymer bulk and in the boundary regions. However, only the free volume fraction of the polymer bulk was included in the calculation. Another source of deviation is the low glass transition temperature of the latex membranes. The glass transition temperatures of solvent cast membranes are usually higher than 100°C while those of latex membranes are below 50°C. During pervaporation, the membrane is in the rubbery state, which leads to a significant error when Eqs. (10) to (12) are used to calculate the free volume fractions.

TABLE 8
Experimental and Calculated Permeabilities of Individual Components through the P(MMA–BuA) Latex Membrane at 25°C (permeability × 10^{-3} g/m·h)

	Ethanol		Water		Ratio	
w_f[a]	E[b]	C[c]	E	C	Ethanol	Water
0	0	0	2.13	4.41		4.8
0.15	0.095	0.018	2.38	4.86	5.3	4.9
0.30	0.026	0.0512	2.85	3.70	0.5	7.7
0.50	0.110	1.376	2.95	2.41	0.8	12.3
0.75	0.475	1.975	2.94	1.68	2.4	17.5
0.95	2.501	2.082	2.33	0.27	12.0	86.3
1.0	5.520	1.428	0	0	38.7	

[a] Ethanol weight fraction in feed.
[b] Experimental value.
[c] Calculated value.

CONCLUSIONS

The Yeom–Huang model, which is a free volume approach developed to characterize the pervaporation of solvent cast membrane systems, is employed for modeling and estimation of the pervaporation property of latex membranes. In this approach the detailed latex membrane structure is disregarded and the membrane is treated as a homogeneous system. By using the free volume parameters of the pure component and the equilibrium sorption data, the permeabilities of the individual components in a binary liquid mixture are predicted. The calculated permeabilities are shown to be reasonable estimates of the experimental results. The deviations may be partly due to the assumptions and simplifications made during modeling.

NOTATIONS

a_i	chemical activity of component i
A_{di}	free volume parameters
B_{di}	free volume parameters
c	concentration
D	diffusion coefficient
D_i	diffusion coefficient of the permeant i
D_{i0}	diffusion coefficient of the permeant i in the membrane in limit of no swelling of the membrane
$(D_T)_i$	thermodynamic diffusion coefficient
$f(0, T)$	free volume fraction of the polymer
$f(v_i, T)$	free volume fraction of the membrane system at temperature T
J	permeation rate
l	membrane dry thickness
P	permeability
R	gas constant
T	temperature in Kelvin scale
T_g	glass transition temperature
v	volume fraction
v_f	specific volume of the liquid at any temperature T
v_0	specific volume of the liquid extrapolated to the temperature 0 K without phase change
x_R	relative distance
$\beta_i(T)$	a proportional constant relating the amount of free volume increased by the diffusion species i
ϕ	sorption ratio or volume fraction in equilibrium sorption
ϕ_c	degree of crystallinity of the membrane

χ_{ip}	interaction parameter characterizing the interactions between penetrant and the polymer membrane

Subscript

e	ethanol
i, j	type of feed component
p	polymer
s	solvent

Superscript

s	sorption
0	ideal sorption

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