

A Comparative Study on the Free Volume Theories for Diffusivity Through Polymeric Membrane in Pervaporation Process

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ABSTRACT: In this work, free volume theories are coupled with a thermodynamic model and generalized Fick's law to develop a mass transfer model based on solution-diffusion mechanism for pervaporation process with a hydrophobic polymeric membrane. The Wesselingh, Fujita and Vrentas-Duda's theories are used to calculate concentration-dependent diffusion coefficient of permeants inside polydimethylsiloxane membrane. The sorption and pervaporation experiments on aqueous ethanol solutions are performed to validate the sorption and pervaporation models. The results reveal that the proposed models are able to predict influences of feed concentration and temperature as well as permeate-side pressure on partial fluxes through the membrane. The comparative investigation indicated that Wesselingh's free volume theory underestimated the diffusion coefficients inside the membrane and the accuracy of the model used this theory is very low for prediction of the permeation flux. Generally, Fujita and Vrentas-Duda's theories are found to be much more accurate especially for dilute aqueous feed solutions. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40581.

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INTRODUCTION

The solution-diffusion model has generally been employed to describe the mass transfer through nonporous membranes in the pervaporation process, because the fundamental equations describing transport in this process can be derived from simple, basic principles without resource to process-specific factors. These equations provide an accurate description of the behavior of these membranes and the dependence of membrane transport on pressure, concentration, and the like.¹ In this mechanism, the mass transfer occurs in three consecutive steps, including (i) preferential sorption of species into the membrane at the feed/membrane interface, (ii) selective diffusion of species across the membrane, and (iii) desorption of vapor penetrants into the permeate phase at the membrane/permeate interface.

The selective sorption and diffusion are major steps in the pervaporation process and determine the partial fluxes as well as desirable permeant selectivity. Fick's law^{2–5} and the Maxwell–Stefan model^{5–7} are often applied to describe the diffusive mass transfer of species inside the polymeric membrane. However, the estimation of diffusion coefficient for penetrants through the membrane is perhaps the critical point in these equations as various

approaches have been chosen to predict the diffusion coefficient values. For example, some authors have utilized the constant values for the penetrant diffusion coefficients through the membrane.^{2,4,8–10} The constant values have good agreement when the feed solutions are much diluted.^{4,8–10} Nonetheless, for more concentrated systems, using diffusion coefficient equations that are dependent on the species concentrations through the membrane are necessary to predict the diffusion behaviors appropriately.^{11–13} For this purpose, several empirical models^{5,14–21} and various free volume theories such as Fujita,²² Vrentas–Duda,²³ and Wesselingh²⁴ have been proposed for the concentration dependent diffusion coefficients through the polymeric membrane. The use of empirical models are restricted to a given feed solution and membrane, which were used in the experiments to estimate the required adjustable parameters of the model, therefore resulting in drawbacks that limit the application of the empirical models.

The free volume theory was developed by Doolittle²⁵ to express the temperature dependency of the viscosity of the liquid normal paraffins. Various models have been developed based on the free volume theory. This theory was then introduced by Fujita²² for the polymeric systems. According to the free volume

theory, the permeant molecules diffuse through the free volumes in the polymer matrix that are randomly created by thermal motions of polymer chains in amorphous regions. Besides, free volume theories are able to predict the diffusion coefficients for a wide variety of pervaporation systems. The earlier studies reveal that the predicted results by the free volume theories are in good agreement with the experimental observations.²⁶ The free volume theories have extensively been employed to estimate the diffusion coefficient of permeants through the polymeric membranes.^{3,7,11–13,27–31} For instance, Yeom and Huang¹³ utilized Fujita's free volume theory in order to determine the diffusion coefficients of water and ethanol through the PVA membrane. Peng et al.²⁷ also used Fujita's free volume theory to model the diffusion of benzene from aqueous solutions through the PDMS membrane. Furthermore, Wesselingh's free volume theory was used by Habeych et al.³¹ and Raisi et al.⁷ to predict the diffusion coefficients of volatile compounds through the starch-based and PDMS membranes, respectively. Chen and Chen¹² employed Vrentas–Duda's free volume theory and Fick's law for pervaporation separation of ethylene glycol from water by the PVA membrane. Also, Yang and Lue⁵ as well as Raisi et al.²⁸ applied Vrentas–Duda's free volume theory for determining the diffusion coefficients of water and ethanol through the PDMS membrane. A search in the literature reveals that there are no comparative studies on efficiency and predictability of the free volume theories for description of the diffusion coefficients through the polymeric membranes in the pervaporation process.

In the previous study,¹¹ we developed a predictive mass transfer model for the pervaporation process based on the solution-diffusion model using constant and concentration dependent diffusion coefficients and it was found that the diffusion coefficient dependencies on the penetrants concentration must be taken into account and it is reasonable to ignore the temperature variation through the membrane. The aim of this work is to perform a comparative study on the accuracy and predictability of three free volume theories including Fujita, Wesselingh, and Vrentas–Duda's theories, for the diffusivity of components in the pervaporation process with a hydrophobic membrane. For this purpose, a thermodynamic model, generalized Fick's law by considering the coupling of fluxes and the free volume theories are employed to develop a mass transfer model. The finite element method is employed to solve the mass transfer equations to obtain the partial fluxes. Besides, by modifying the boundary condition at the membrane/permeate interface with respect to the previous work,¹¹ the proposed model is able to predict the influences of permeate-side pressure further to two key operational parameters, that is, feed ethanol concentration and feed temperature, on the pervaporation performance. Finally, the pervaporation experiments are conducted using aqueous ethanol solutions with a commercial composite PDMS membrane to validate the mass transfer model.

THEORY

Mass Transfer Model Development

In this study, a predictive mass transfer model is developed for the hydrophobic pervaporation with the following assumptions. (i) The solution-diffusion mechanism is assumed to hold true. (ii) The permeation through the membrane is considered isothermal, steady-

state and one dimensional. (iii) The mass transport resistances in the feed-side boundary layer and the support layer of the composite membrane are negligible.^{28,32} (iv) The pressure gradient is neglected in respect to the component activity gradient contribution.

The mass transfer governing equations through the membrane for each species in the binary feed mixture regarding the proposed assumptions and by considering the effect of coupling of fluxes to thoroughly predict the behavior of components through the diffusion, are written as:¹¹

$$\frac{d}{dx} \left[\phi_i D_i \left(\sum_{j=1}^2 \frac{\partial \ln a_i}{\partial \phi_j} \frac{d\phi_j}{dx} \right) \right] = 0 \quad (1)$$

where ϕ and x are volume fraction of components and the diffusion direction, respectively. a is activity of components, which is determined by extended Flory-Huggins theory for the ternary polymeric system.^{2,33} D denotes the diffusion coefficient of components through the membrane. Chen and Chen¹² proposed that for the polar–polar feed solution, the diffusion coefficient of the component through the membrane includes self diffusivity, component diffusivity at infinite dilution solution and basic diffusivity of component inside the polymeric membrane. In this work, the ternary diffusion coefficients considering the interaction parameters of penetrants and polymer during permeation are applied. The relationship between the diffusion coefficients is expressed by the Vignes equation as follows:³⁴

$$D_i = \prod_{j=1}^3 D_{ij}^{\phi_j} \quad (2)$$

where for a water (1)/ethanol (2)/membrane (3) system, D_{11} and D_{22} are self-diffusivity and they are determined using Lee's self-diffusivity equations. Lee et al.³⁵ developed a corresponding state model to determine the self-diffusivity for liquids. The self-diffusivity is estimated just by knowing thermodynamic properties such as critical temperature, pressure, molar volume, and density as well as molecular weight. Besides, D_{12} and D_{21} are binary diffusivity at infinite dilution solution, which is estimated by the Wilke–Chang equation. This equation is a general correlation for estimating the diffusion coefficients in the diluted solutions with reasonable precision. To estimate the diffusivity, physical properties such as viscosity, temperature, and molecular weight would be necessary.³⁶ Finally, D_{13} and D_{32} are the diffusion coefficients inside the membrane that are determined by the free volume theories.

Diffusion Coefficients Inside the Membrane

Wesselingh's Free Volume Theory. Wesselingh and Bollen²⁴ proposed the extended free volume theory for multicomponent mixtures. They found that the free volume is accessible for any component according to its surface fraction. The diffusion coefficient of components inside the membrane is given by:

$$D_{i3} = \frac{RT}{\zeta_{i3}}, \quad (3)$$

where

$$\zeta_{i3} = \frac{\zeta_{i,\text{eff}} \zeta_{3,\text{eff}}}{\sum_{j=1}^3 x_j \zeta_{j,\text{eff}}} \quad (4)$$

Table I. The Free Volume Parameters of Permeating Components in the PDMS Membrane for Fujita's Free Volume Theory

Penetrant	B	$R \times A_d$
Ethanol	0.6593	2.30×10^{-10}
Water	0.7076	1.30×10^{-10}

$$\xi_{i,\text{eff}} = 2A\sqrt{3kT\rho^*d_i} \exp\left(0.7\frac{v_i^*}{v_{Fi}}\right) \quad (5)$$

$$\rho^* = \sum_{j=1}^3 x_j \rho_j^* \quad (6)$$

$$d_i = \left(\frac{v_i^*}{A}\right)^{1/3} \quad (7)$$

$$v_{Fi} = v_i - v_i^* \quad (8)$$

and

$$v_i^* = 0.289v_{ci} \quad (9)$$

where ξ_{i3} and $\xi_{i,\text{eff}}$ are friction coefficient and effective tracer friction coefficient, respectively, A , R , and k are Avogadro, gas, and Boltzman constant, respectively, ρ_i^* and ρ^* are maximum density of component and mixture i , respectively, d_i is molecular diameter, v_{Fi} and v_i are the free volume and molar volume of each component, respectively, v_{ci} and v_i^* are the critical volume and minimum volume of component i , respectively and T is absolute temperature.

Fujita's Free Volume Theory. According to the Fujita free volume theory,²² the remarkable assumption for estimating the diffusion coefficient for small size permeating molecule in amorphous polymeric membrane is that the molecular weight of the penetrant is equal to molecular weight of a jumping unit of polymer chain. In the other word, Fujita free volume theory ignores the effect of solvent size. In practice, this assumption limits the application of the Fujita free volume theory for organic solvents as they have molecular weight approximately equal to the molecular weight of polymer jumping unit chain. Hence, the diffusion coefficient of component i through the membrane is expressed as:

$$D_{i3} = RT A_{d_i} \exp\left(\frac{-B_{d_i}}{f(\phi_i, T)(1-\phi_c)}\right) \quad (10)$$

where A_d and B_d are parameters related to the size and shape of penetrant molecules as well as $f(\phi_i, T)$ and ϕ_c being the free volume fraction and crystallinity of the polymeric membrane. A generalized parameter B_i is defined as:

$$B_i = \frac{B_{d_i}}{1-\phi_c} \quad (11)$$

Thus, eq. (10) is rearranged as the following equation, which is called *Fujita-I* during this study:

$$D_{i3} = RT A_{d_i} \exp\left(\frac{-B_i}{f(\phi_i, T)}\right) \quad (12)$$

The free volume fraction of the binary system is calculated by the following equation:³⁷

$$f(\phi_i, T) = f(0, T) + \beta_i(T)\phi_i \quad (13)$$

where $f(0, T)$ is the fractional free volume of the pure polymer. For the temperature above the glass transition temperature (T_g) of the PDMS membrane, $f(0, T)$ is determined as:³⁷

$$f(0, T) = 0.025 + 4.8 \times 10^{-4}(T - T_g) \quad (14)$$

The proportional constant ($\beta_i(T)$) is determined as:

$$\beta_i(T) = f(0, T) - f(1, T) \quad (15)$$

The values of $f(1, T)$ for ethanol and water have been given by Yeom and Huang.¹³ A_d and B can be obtained from steady-state pervaporation of the single component.¹² As there are two single component fluxes at two different temperatures and there are two free volume parameters to determine, there are two nonlinear equations to solve. The MATLAB function "fsolve" is applied to find the parameters. The obtained parameters are given in Table I.

When a binary liquid diffuses through the membrane, the system includes three components that is polymer free volume itself as well as an increase in free volume owing to the plasticizing actions of two liquids. Thus, according to the free volume theory, the diffusion coefficient (D_{i3}) in the ternary system can be obtained by the following equation, which is called *Fujita-II* during this study.¹³

$$D_{i3} = RT A_{d_i} \exp\left(\frac{-B_i}{f(0, T) + \beta_i(T)\phi_i + \beta_j(T)\phi_j}\right) \quad (16)$$

For estimating these parameters, when the component j is removed from the system, the diffusion coefficient for component i can be obtained as:

$$D_{i3} = RT A_{d_i} \exp\left(\frac{-B_i}{f(0, T) + \beta_i(T)\phi_i}\right) \quad (17)$$

The required parameters will be acquired with the same procedure as it is implemented for adjusting the parameters of *Fujita-I*. The pure experimental permeabilities and the predicted values are shown in Figure 1.

Vrentas-Duda's Free Volume Theory. In contrast to Fujita free volume theory, since penetrant molecules such as ethanol, have significantly smaller molecular weight in comparison to that of jumping unit of polymer chain, Vrentas et al.^{38,39} proposed a new version of free volume theory considering the effect of solvent size. On the basis of Vrentas-Duda's free volume theory for the ternary system, the penetrants/membrane diffusion coefficient is given by:^{38,39}

$$D_i = D_{0i} \exp\left(\frac{-E_i}{RT}\right) \exp\left(\frac{-w_i \hat{V}_i^* + \left(\frac{\xi_{ij}}{\xi_{ip}}\right) w_j \hat{V}_j^* + \xi_{i3} w_3 \hat{V}_3^*}{\hat{V}^{FH} / \Gamma}\right) \quad (18)$$

$$\hat{V}^{FH} / \Gamma = \sum_{i=1}^3 w_i \frac{k_{I,i}}{\Gamma} (k_{II,i} - T_{g,i} + T) \quad (19)$$

In the aforementioned equations, E_i is the critical energy, in which a molecule needs to overcome the attractive forces neighboring molecules and Γ is an overlap factor which accounts for shared free volume. \hat{V}_i^* and \hat{V}_3^* are the specific critical hole free volume of component i and 3, respectively required for the jump. w_i and w_3 are the weight fraction of component i and 3. ξ denotes the ratio of critical molar volume of solvent jumping unit to that of

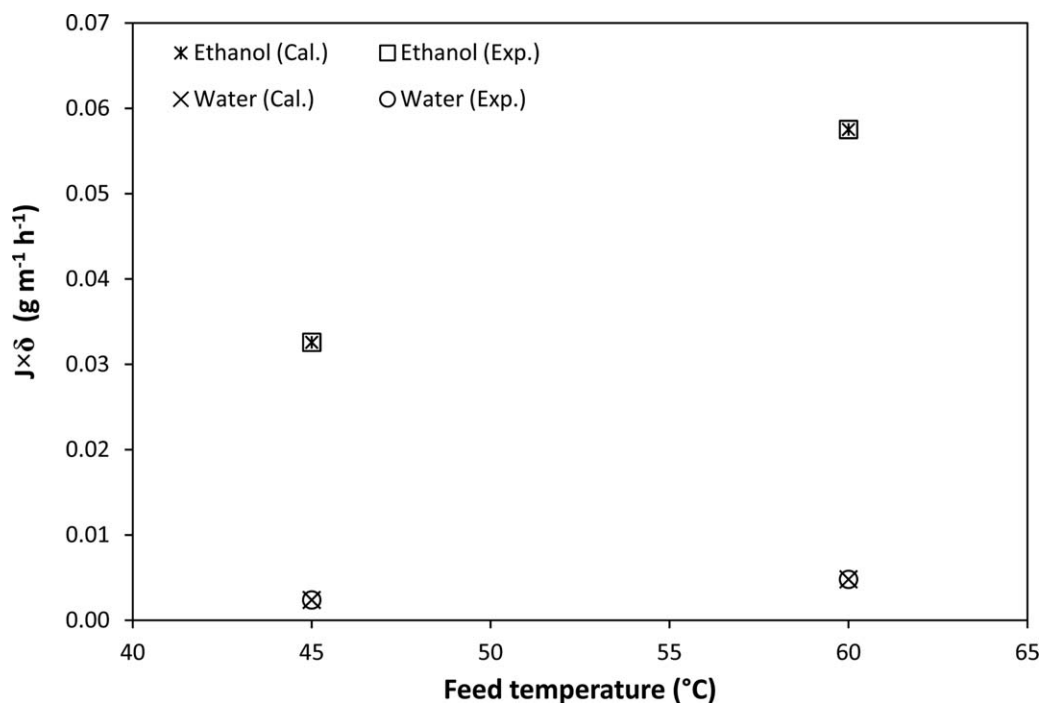


Figure 1. The experimental and predicted permeability values of the pure component permeation at different temperatures.

polymer jumping unit. $k_{f,i}$ and $k_{f,i}$ are solvent free volume parameters while $k_{f,3}$ and $k_{f,3}$ are free volume parameters for the polymer. D_{0i} is a zero concentration diffusion coefficient of the penetrants through the membrane in a binary system and is calculated using the method proposed by Mafi et al.¹¹ The parameters of eqs. (18) and (19) for some solvents and polymers can be found in the literature.^{39,40} The required free volume parameters for the system of water/ethanol/PDMS membrane are presented in Table II. In the development of the Vrentas-Duda's free volume theory, the contribution of the polymer self-diffusion coefficient is assumed negligible.³⁸

Boundary Conditions

For solving the nonlinear differential equations [eq. (1)] for both penetrants, two boundary conditions are required. The first boundary is at the feed/membrane interface. It can be obtained by taking into account a thermodynamic equilibrium between the feed mixture and the PDMS membrane at the interface. It can be inferred from the fundamental relations of thermodynamic that the iso-activity criterion for each species must be confirmed as:

$$a_i^f = a_i^m \quad (20)$$

The activities of the component in the feed mixture are determined using the UNIFAC group-contribution method⁴² and the component activities in the PDMS membrane are also estimated by the extended Flory-Huggins theory [eqs. (1)–(5) and eq. (34) in Mafi et al.¹¹]. After determining the interaction parameters of the extended Flory-Huggins theory, the activity of components in the membrane can be easily calculated by adding $\sum_{i=1}^3 \phi_i = 1$ to eqs. (1) and (2) in Mafi et al.¹¹ and by solving the set of nonlinear equations using the MATLAB function

“*fsolve*,” the volume fraction of components in the membrane at the feed-side (ϕ_i^f) is determined.

The second boundary is at the membrane/permeate interface. By considering an assumption that the thermodynamic equilibrium is reached at the interface between the permeate phase and the membrane phase, the activities of the component in both phases will be equal. Besides, the components are vapor at the permeate as well as the pressure is very low in this region and the vapors behave ideally at very low pressure. Thus, the following equations can be written in order to find the volume fraction of components in the membrane at the permeate-side (ϕ_i^p):

$$a_i^p = a_i^m \quad (21)$$

where

$$a_i^p = y_i^p \frac{P^p}{P_i^0} = \frac{N_i^{\text{exp}} P^p}{N_{\text{total}}^{\text{exp}} P_i^0} \quad (22)$$

where y_i^p , P_i^0 and P^p are experimental mole fraction, vapor pressure of component i and total pressure at permeate-side, respectively. N_i^{exp} and $N_{\text{total}}^{\text{exp}}$ are partial and total experimental mass

Table II. The Free Volume Parameters for the Water/Ethanol/PDMS System for Vrentas-Duda's Free Volume Theory

Parameter	Water (1) ⁴⁰	Ethanol (2) ⁴¹	PDMS (3) ³⁹
\tilde{V}^* (cm ³ g ⁻¹)	1.072	0.987	0.905
$\frac{k_{f,i}}{T}$ (cm ³ g ⁻¹ K ⁻¹)	2.18×10^{-3}	3.12×10^{-4}	9.32×10^{-4}
$k_{f,i} - T_g$ (K)	-152.29	111.80	-81.00
ξ_{ip}	0.232	0.545	-
E (J mol ⁻¹)	1046.74	789.55 ²⁸	-

fluxes, respectively. The activities of the component in the membrane at permeate-side (a_i^m) are determined using the Flory-Huggins equations for a ternary system.³³

To sum up, two required boundary conditions for eq. (1) are imposed as:

$$\phi_i(x=0) = \phi_i^f \quad (23)$$

$$\phi_i(x=\delta) = \phi_i^p \quad (24)$$

Calculation of Partial Fluxes and Permeate Weight Fraction

Once the governing mass transfer equations are solved simultaneously, the partial fluxes and permeate weight fraction can be obtained. The nonlinear differential equations are solved numerically using the finite element method, and the details of solution procedure are presented elsewhere.¹¹

According to the generalized Fick's law and taking into consideration the effect of the flux coupling, the partial fluxes for component i can be expressed as:^{2,11}

$$J_i = -\rho_i D_i \phi_i \left(\sum_{j=1}^2 \frac{\partial \ln a_i}{\partial \phi_j} \frac{d\phi_j}{dx} \right) \quad (25)$$

where ρ is density and distance independent. Also, the activities derivatives are determined from the extended Flory-Huggins equations.

Moreover, the weight fraction of component i in the permeate can be calculated by:

$$w_i^p = \frac{J_i}{\sum_1^2 J_i} \quad (26)$$

EXPERIMENTAL

To separate ethanol (99.8%, Merck, Darmstadt, Germany) from its aqueous solution by pervaporation, deionized laboratory water is used to produce different feed mixtures. The pervaporation experiments are performed with a commercial composite PDMS/PVDF/PP membrane with active layer thickness of 10 μm , which was kindly supplied by Helmholtz-Zentrum Geesthacht Zentrum für Material und Küstenforschung GmbH (Geesthacht, Germany). The apparatus used in the pervaporation experiment has previously been described in details elsewhere.⁴³ The total flux (J) is calculated using the following equation:

$$J = \frac{W}{S t} \quad (27)$$

where W , S , and t are weight of the collected permeate, membrane area (137.75 cm^2) and time duration of the experiments, respectively.

For investigating the effects of feed concentration on the diffusive fluxes, the pervaporation experiments are conducted for the feed ethanol contents of 0.015, 0.050, 1, 2, 3, 4, 5, 10, 15, 25, and 50 wt % at the feed temperature of 60°C and permeate-side pressure of 1 mmHg. Besides, for the influences of the feed temperature, the experiments are implemented at feed temperatures of 30, 45, and 60°C at permeate-side pressure of 1 mmHg and feed ethanol content of 5 wt %. Finally, two feed ethanol

concentrations of 5 and 50 wt % are chosen to determine the influence of permeate-side pressure (pressures of 1, 10, 20, and 40 mmHg for 5 wt % and pressures of 1, 10, 40, 80 and 100 for 50 wt %) at feed temperature of 60°C. The feed flow rate in all the experiments is fixed at 97.8 kg h^{-1} .

For estimating Fujita's free volume parameters, the single permeations of ethanol and water are conducted at feed temperatures of 45 and 60°C.

Furthermore, the sorption experiments are conducted using a gravimetric procedure²⁸ to measure the amount of water and ethanol sorbed by the PDMS layer of the composite membrane. These experiments are carried out for the feed temperature of 30, 45, and 60°C and the feed ethanol concentration of 0, 2, 5, 25, 50, 70, and 100 wt %. The sorption results are reported as the ratio of the liquid weight sorbed per gram of dry membrane (w^s) as follows:

$$w^s = \frac{w_s - w_d}{w_s} \quad (28)$$

where w_d and w_s denote the weight of dry and swollen membranes, respectively.

RESULTS AND DISCUSSION

Sorption into the Membrane

The sorption levels of ethanol/water mixtures into the pure PDMS membrane were thermodynamically modeled and validated by the swelling experiments. Figure 2 depicts the effects of feed ethanol content on the amount of components taken by the PDMS membrane at feed temperature of 30°C. As shown in Figure 2, both the experimental and modeling results indicate that an increase in the feed ethanol concentration contributes to intensive enhancement of sorbed ethanol in the PDMS membrane. As the applied membrane is hydrophobic and nonpolar, this membrane has a greater tendency to take substances that have a similar physical and chemical nature. Therefore, the more ethanol the feed contains, the more ethanol the PDMS membrane takes. In contrast to the sorption behavior of ethanol molecules, as shown in Figure 2, the water sorption curve shows a maximum indicating that the strong affinity between water and ethanol molecules can overcome the repellent force of the membrane matrix and reaches an equilibrium state. Furthermore, the amount of water taken by the hydrophobic membrane is greater than ethanol sorption at low ethanol concentration in feed solutions. The reason is that, under the same solvent activity, the ethanol will have higher sorption in the PDMS than water molecules. Hence, at low feed ethanol content, the water molecules have higher activity and consequently exhibit higher sorption. Moreover, the plasticization effect exerted by the presence of a small amount of ethanol also enhances the water molecules taken. It can be seen from Figure 2 that coupling of the UNIFAC and Flory-Huggins theories can successfully predict the amount of ethanol and water sorbed into the PDMS membrane for a wide range of feed ethanol concentrations.

Diffusion Through the Membrane

As mentioned earlier, according to the solution-diffusion mechanism, two major impressive steps in the pervaporation are selective sorption and diffusion of the component in the

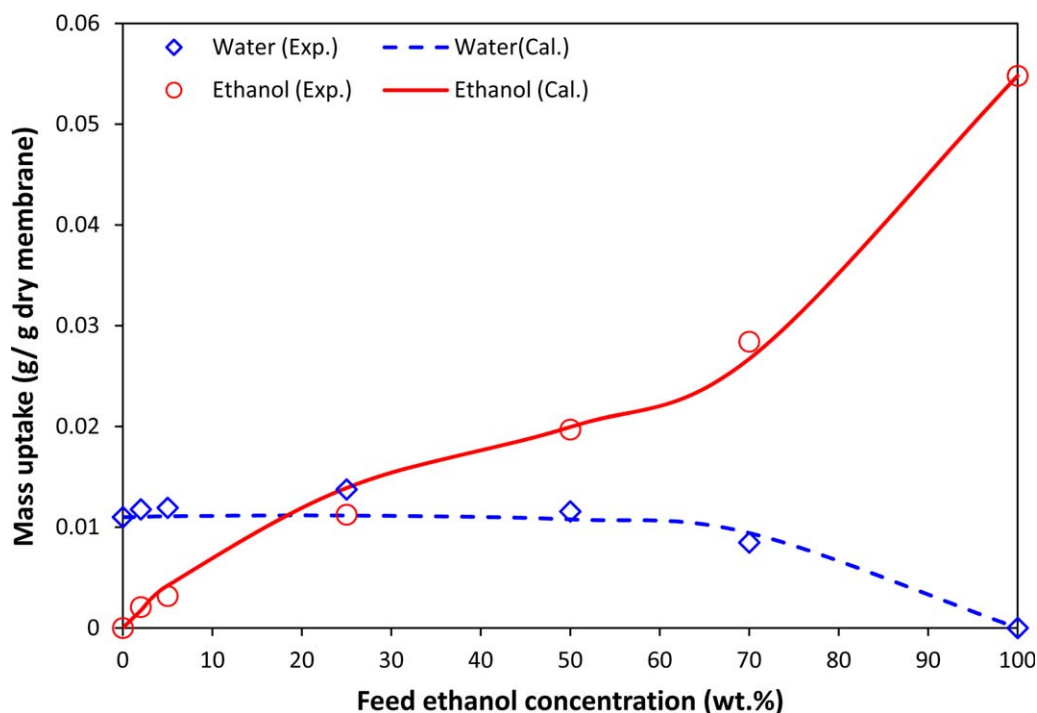


Figure 2. The effect of feed ethanol content on the sorption of ethanol (a) and water (b) in the membrane at feed temperature of 30°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

membrane. Therefore, the feed temperature and ethanol concentration determine performance of the process regarding the sorption and diffusion steps since the membrane swelling and coupling effects as well as the concentration polarization significantly depend on these two operational parameters. Apart from the feed temperature and concentration, permeate-side pressure also affects the pervaporation performance. Variation of the permeate-side pressure may cause either the driving force of the diffusion to become lower or greater. Consequently, it directly impresses the diffusion step in the mechanism. Therefore, the effects of these operational variables are investigated via the proposed mass transfer model and experimental data in the following.

Figure 3 illustrates the feed ethanol concentration effects on partial and total fluxes at a feed temperature of 60°C. Once the feed ethanol content varies from 0.015 to 50 wt %, the ethanol flux enhances as shown in Figure 3(a). Also, the ethanol diffusive flux linearly depends on feed concentration through the PDMS membrane according to the predicted results and experimental observations. In earlier studies, the same behavior has been observed for ethanol permeation through the PDMS membrane.^{44–46} The increasing trend of ethanol flux can be explained regarding the driving force of diffusion in the PDMS membrane. The chemical potential of the component obviously depends on the feed concentration. The chemical potential enhances through the PDMS once the feed ethanol content goes to a higher level. In contrast, the partial fluxes are linearly dependent on the chemical potential, and therefore, an enhancement in the chemical potential results in increment of the partial flux. Besides, as mentioned earlier, by increasing the feed ethanol content, the amount of components taken by the

PDMS is also boosted and leads to an increase in the driving force and component concentration in the membrane. Increasing the component concentration in the membrane may cause membrane swelling which facilitates the diffusion of components, consequently leading to enhancement of the partial fluxes. As can be seen from Figure 3(a), Wesselingh's free volume theory underestimates the ethanol flux in comparison to the experimental data from 0.015 to 50 wt % ethanol concentration. In contrast to the Wesselingh theory, for diluted feed solutions (0.015–5 wt % ethanol concentration), the predicted values of the ethanol flux by both *Fujita-I* and *Fujita-II* are in good agreement with the experimental observations. Nonetheless, the differences between the predicted and experimental ethanol fluxes increases at higher feed ethanol concentrations for both Fujita's free volume models. Furthermore, *Fujita-II* always predicts the greater amount for the flux when compared with *Fujita-I*, as the calculated diffusion coefficients for ethanol by *Fujita-II* will be higher than *Fujita-I*. One explanation could be that *Fujita-II* considers the coupling effects for estimating the diffusion coefficients, and the coupling effect can be seen in the denominator of eq. (16). Since in eq. (16), the total free volume includes polymer free volume itself as well as an increase in free volume owing to the plasticizing actions of two liquids, as a result of enhancing free volume, the diffusion coefficients will be estimated as greater for permeating molecules in respect to eq. (12) in which the coupling effect is ignored. In contrast, the estimated values by Vrentas-Duda's free volume theory are also in good agreement with the experimental results when the feed solution is diluted. Similar to the Fujita theory, with an increase in feed concentration, the predicted values deviate from the experimental data, but these deviations are lower than that of Fujita's predictions in the whole range of concentrations.

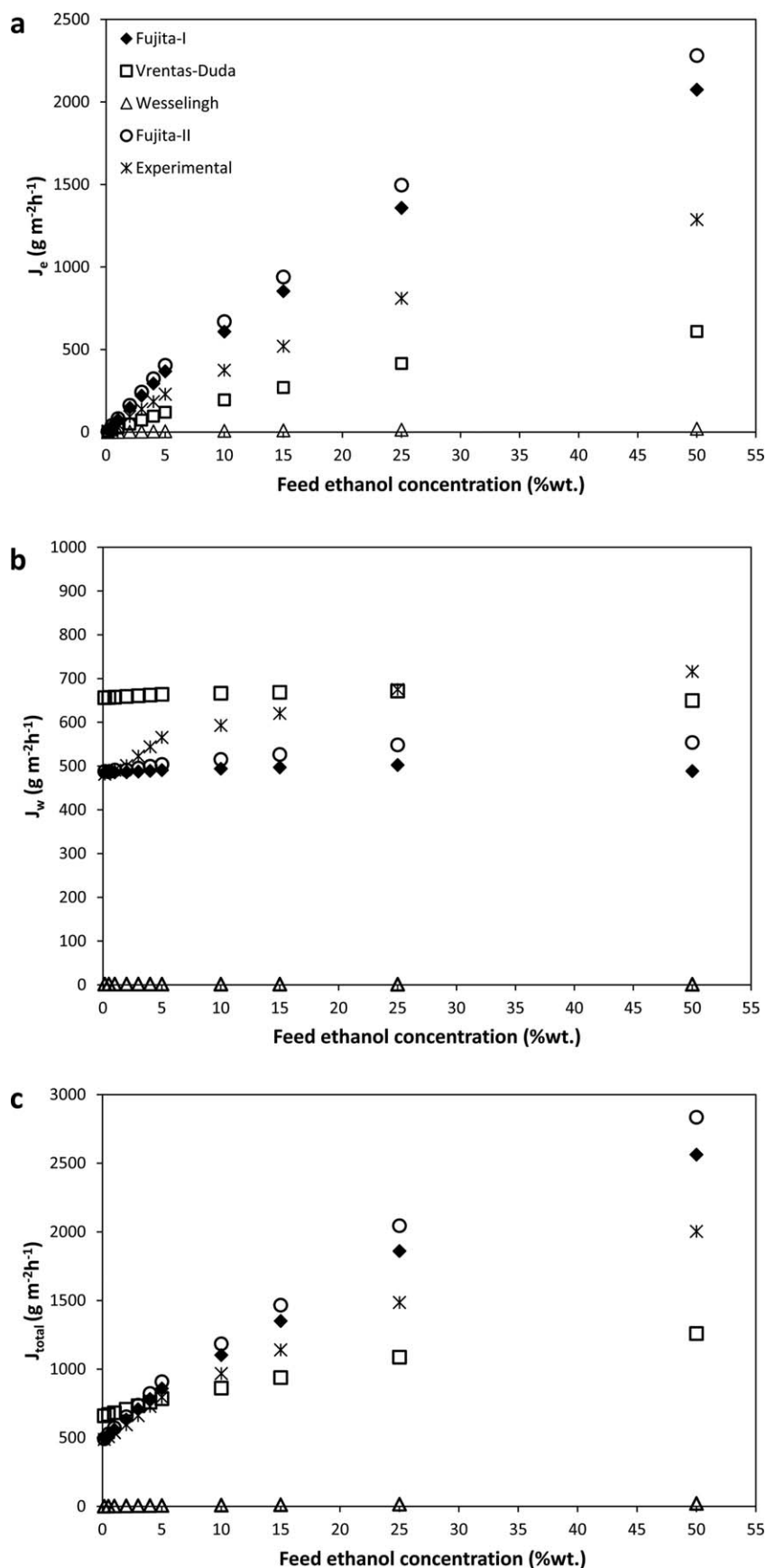


Figure 3. The effect of the feed concentration on the pervaporation performance of ethanol separation at 60°C and permeate-side pressure of 1 mmHg: (a) ethanol flux, (b) water flux, (c) total flux.

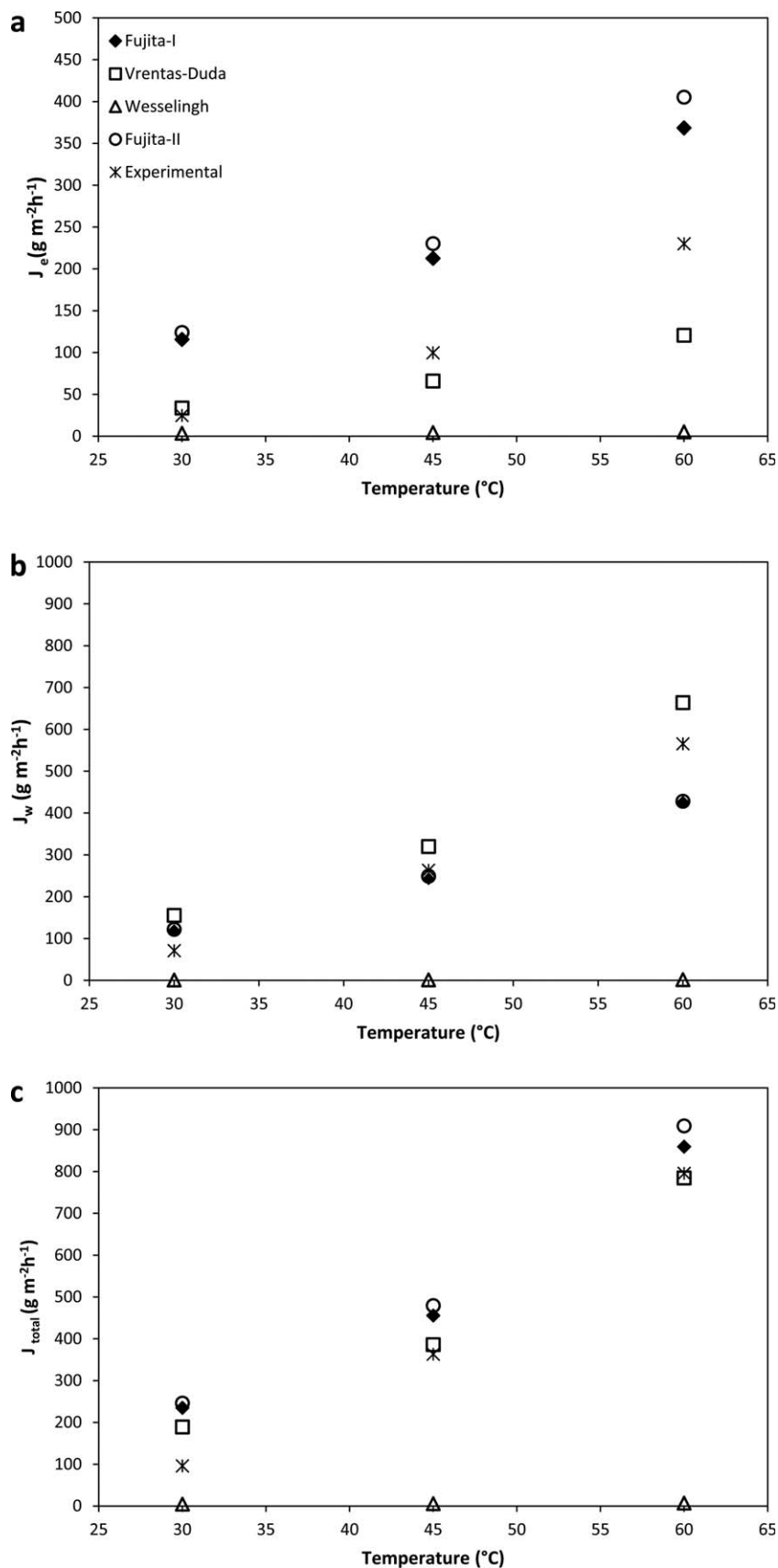


Figure 4. The effect of the feed temperature on the pervaporation performance of ethanol separation for a 5 wt % feed solution at permeate-side pressure of 1 mmHg: (a) ethanol flux, (b) water flux, (c) total flux.

The water flux also enhances slightly in comparison to the increasing trend of the ethanol flux with the enhancement of feed concentration as illustrated in Figure 3(b). The experimental observation shows that variations in the feed concentration from 0.015 to 50 wt % lead to an increase in the water partial flux from 482 to 716 $\text{g m}^{-2} \text{h}^{-1}$. When the ethanol concentration increases or the water concentration decreases in the feed solution, the lower sorption of water molecules into the membrane occurs as depicted in Figure 2. On the contrary, higher ethanol sorption into the membrane due to higher ethanol concentration in the feed solution leads to the membrane swelling, and thus the water molecules can easily pass through the swollen membrane. As a result, an increase in the feed ethanol content results in decreasing water sorption and increasing water diffusion and consequently these two adverse phenomena cause a slight increase in the water partial flux through the membrane. As can be seen from Figure 3(b), Wesselingh's free volume theory underestimates the water flux values compared with the experimental data similar to the ethanol flux prediction. In contrast, Vrentas-Duda's predictions for the water flux in dilute feed solution differ significantly from the experimental one even though the model can predict the slightly increasing trend. Apart from concentrated feed solution (5–50 wt %) the predicted values are in good agreement with the experimental data. *Fujita-I* and *Fujita-II* can successfully predict the amount of water flux when the feed mixture is diluted. This could be related to the approach chosen to adjust the required parameters as the single permeation pervaporation data are used for the adjusting parameters. When the feed ethanol content is low, the water concentration is inversely high and near the pure water. Therefore, it is expected that the prediction would be satisfying. As the ethanol concentration increases, the predicted values deviate from the experimental observations. As can be seen from Figure 3(b), the predicted values by *Fujita-II* are always greater than that of *Fujita-I* because as mentioned earlier the coupling effect considered by *Fujita-II* results in higher diffusion coefficient estimations, and consequently a greater amount of flux prediction.

Total flux also increases as the ethanol content in the feed enhances [Figure 3(c)] because both partial fluxes of water and ethanol increase with an enhancement in concentration. As can be seen in Figure 3(c), *Fujita-I* and *Fujita-II* are capable of predicting the total flux in the range from 0.015 to 10 wt % successfully, but at a higher concentration, the predicted values deviate from the experimental data. Although Vrentas-Duda's predicted values deviate from the experimental observations in the range from 0.015 to 2 wt %, it is able to efficiently predict the total flux when the feed concentration is between 3 and 15 wt %. For higher concentration, the values differ from the experimental data similar to the *Fujita* theory. Similar to the ethanol flux and water flux, Wesselingh's theory cannot predict the total fluxes accurately.

Figure 4 depicts the influences of feed temperature on the separation performance of the PDMS membrane for a 5 wt % ethanol aqueous solution. The partial and total fluxes increase as the feed temperature enhances. According to the free volume theory in the polymeric membrane, there are several free volumes between

the polymer chains in the polymeric matrix made by segmental motions of the polymer chain in the amorphous regions. The permeating components diffuse through these voids in the polymeric membrane. By increasing the feed temperature, the segmental motions of the polymeric chains boost, and thereby the void ways for the diffusion become more available. Thus, the diffusion rate of the individual permeating molecules increases, leading to a high permeation flux. Furthermore, the increasing behavior of fluxes with an increment in the feed temperature is attributed to changes in the driving force with temperature. Once the feed temperature enhances, the vapor pressure of pure penetrants in the feed solution increases and this leads to an enhancement in the driving force and as a result the diffusive partial fluxes enhance. The increasing behavior for fluxes with temperature enhancement has been reported in other investigations.^{44–47} As can be seen from Figure 4(a), with an enhancement in the feed temperature at the moderate feed ethanol concentration of 5 wt %, Wesselingh's theory underestimates the value of ethanol flux, whereas the *Fujita-I* and *Fujita-II* theories overestimate. The difference between predicted results of these theories will be bigger once the feed temperature increases. However, Vrentas-Duda's theory predicts the amount of ethanol flux relatively well. Figure 4(b) reveals that Wesselingh's theory is not able to predict the effects of feed temperature on the water flux further than the ethanol partial flux, whereas *Fujita-I*, *Fujita-II* and Vrentas-Duda's theories can give comparatively good predictions. The same scenario can be observed for total flux. As can be seen in Figure 4(c), the Vrentas-Duda's predicted values are in good agreement with the experimental observations.

The effects of permeate-side pressure on the fluxes and permeate concentration are shown in Figure 5. Both total flux and partial fluxes decrease once the permeate-side pressure enhances. Any rise in this pressure results in an increase of the activities of permeants in the downstream layer of the membrane. Figure 5(a) shows the permeate-side pressure effects on the ethanol flux for two feed ethanol concentrations of 5 and 50 wt % at a temperature of 60°C. For 5 wt % feed ethanol concentration, *Fujita-I* and *Fujita-II* as well as Vrentas-Duda's free volume theory estimate the ethanol flux relatively well in comparison to the experimental data but once the permeate-side pressure increases, the accuracy of Vrentas-Duda's theory decreases whereas it is observed that *Fujita*'s prediction is in good agreement with the experimental data. Nonetheless, once the feed ethanol concentration enhances, the accuracy of models diminishes and the predicted values by the Vrentas-Duda theory approach to the experimental data by increasing the permeate-side pressure. The same trends as the ethanol flux can be observed for the total flux in Figure 5(c). For the water flux in Figure 5(b), when the feed ethanol concentration is low, good accuracy can be seen for *Fujita*'s theory, as the pure water permeation is used for adjusting the required parameters. For this reason, once the feed ethanol content enhances, a greater deviation from the experimental data can be seen. For diluted feed solutions, *Fujita*'s theory has good predictions for permeate-side pressure in the range from 1 to 20 mmHg. For 40 mmHg, the models predicted values differ significantly from the experimental data. The reason could be related to the mass transfer model development, as the effects of pressure

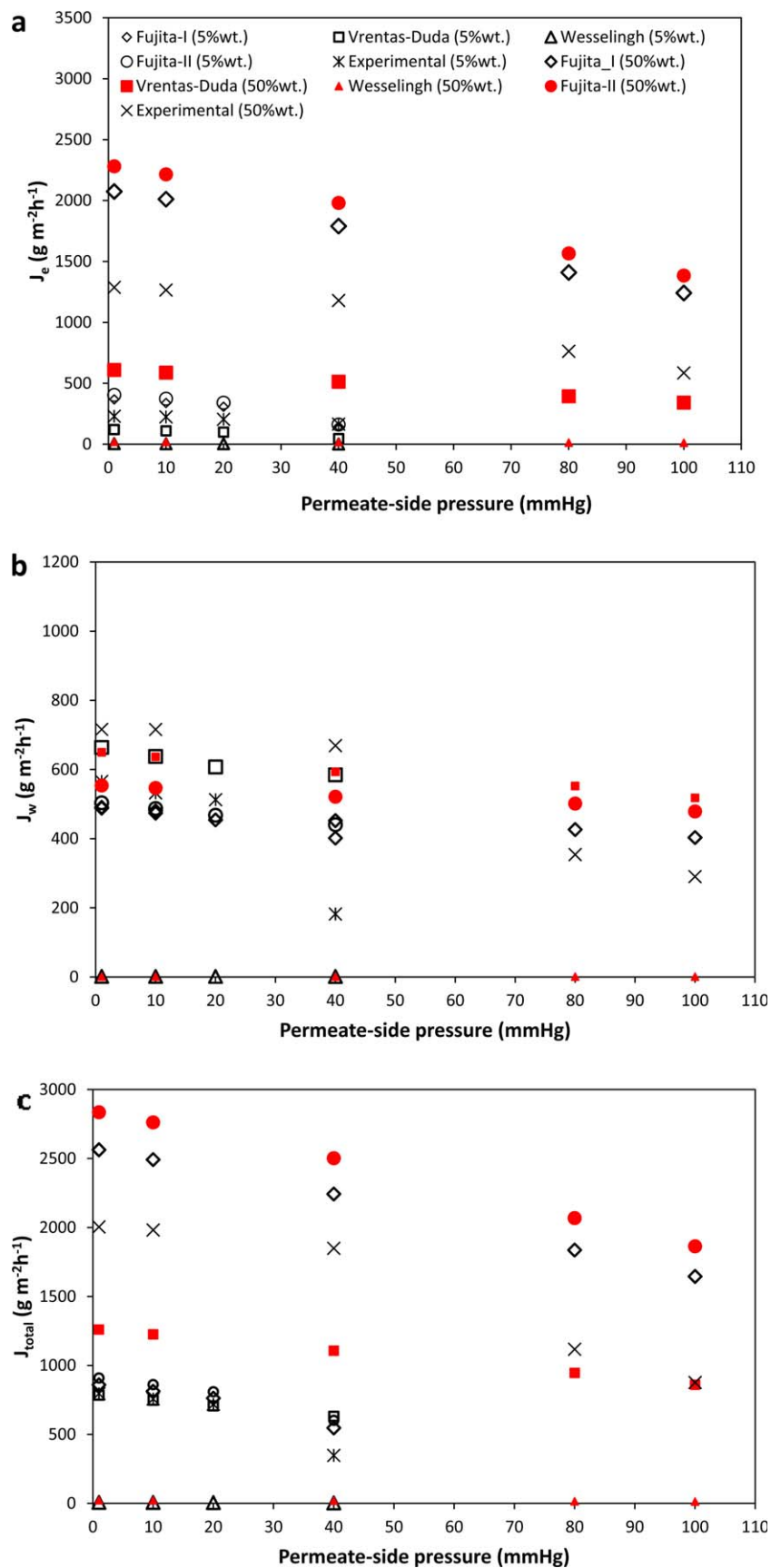


Figure 5. The effect of the permeate-side pressure on the pervaporation performance of ethanol separation for 5 and 50 wt % feed solutions at 60°C: (a) ethanol flux, (b) water flux, (c) total flux. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

gradient across the membrane in respect to the activity gradient are ignored, and therefore, for this huge impact of permeate-side pressure, modifying the boundary conditions is not enough. When the feed ethanol content enhances, Vrentas-Duda's theory can predict the values better than that of Fujita's theory for the permeate-side pressure in the range from 1 to 40 mmHg, whereas the predicted values by Fujita's theory surpass Vrentas-Duda's at higher permeate-side pressure.

CONCLUSIONS

Various free volume theories including Wesselingh, Fujita, and Vrentas-Duda's were employed to develop a mass transfer model for the hydrophobic pervaporation process based on the solution-diffusion theory using a thermodynamic model and generalized Fick's. A comparative investigation was performed on the accuracy and predictability of the theories for the diffusivity inside the membrane. The results showed that the predicted values of the ethanol flux by both *Fujita-I* and *Fujita-II* and Vrentas-Duda's theory were in good agreement with the experimental observations for the dilute feed solutions. Nonetheless, by increasing the feed concentration, the predicted values by Vrentas-Duda's theory deviate from the experimental data, but these deviations were lower than that of Fujita's predictions in the entire range of concentrations. On the contrary, Vrentas-Duda's predictions for the water flux in the dilute feed solution differ significantly from the experimental one even though the model can predict a slightly increasing trend. For the concentrated feed solution, the predicted values by Vrentas-Duda's theory were in good agreement with the experimental data. Finally, it can be concluded that the approach used to calculate the diffusion coefficient of the permeants inside the membrane had a significant effect on the mass transfer model developed for the hydrophobic pervaporation. The accuracy of the model that used Wesselingh's theory was very low for prediction of the permeation flux and permeate concentration. Although the accuracy of the mass transfer model based on Fujita and Vrentas-Duda's theories changed with variations in operating conditions, the predicted values by these theories had relatively good agreement with the experimental observations. Therefore, more modifications should be performed on the free volume theories to exactly predict the diffusivity through the polymeric membranes.

NOMENCLATURE

A	AVOGADRO constant
A_d	free volume Parameter
a_i	activity of component i
B	free volume Parameter
D_i	the Total Diffusion coefficient of component ($\text{m}^2 \text{s}^{-1}$)
D_{0i}	zero concentration diffusion coefficient of component i ($\text{m}^2 \text{s}^{-1}$)
D_{ii}	self-diffusivity of component i ($\text{m}^2 \text{s}^{-1}$)
D_{ij}	binary diffusivity at infinite dilution solution ($\text{m}^2 \text{s}^{-1}$)
D_{i3}	diffusion coefficient of component i into the membrane ($\text{m}^2 \text{s}^{-1}$)
d_i	molecular diameter (m)
F	fractional free volume
E_i	the critical energy of component i (J mol^{-1})
ΔG^E	excess Gibb's free energy (J mol^{-1})

J_i	mass flux of component i ($\text{kg m}^{-2} \text{s}^{-1}$)
K	Boltzman constant
$k_{L,i}$	free volume parameter of component i ($\text{cm}^3 \text{g}^{-1} \text{K}^{-1}$)
$k_{II,i} - T_{g,i}$	free volume parameter of component i (K)
N_i	molar flux of component i ($\text{kmol m}^{-2} \text{s}^{-1}$)
P	pressure of the system (bar)
P^0	vapor pressure (bar)
R	gas universal constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
S	area of the membrane (m^2)
T	absolute temperature (K)
T_g	glassy temperature (K)
T	time duration of experiment (h)
\hat{V}_i^*	specific hole free volume of component i ($\text{cm}^3 \text{g}^{-1}$)
\hat{V}_i^{FH}	average hole free volume per gram of component i ($\text{cm}^3 \text{g}^{-1}$)
v_i	molar volume ($\text{m}^3 \text{mol}^{-1}$)
v_{Fi}	free volume of each component
v_i^*	minimum volume component i ($\text{m}^3 \text{mol}^{-1}$)
v_{ci}	critical volume of component i
W	weight of collected permeate (g)
w_d	weight of dry membrane (g)
w_s	weight of swollen membrane (g)
w_i	weight fraction of component i
w^s	ratio of the liquid weight sorbed per gram of dry membrane
X	penetration direction (m)
y_i	experimental mole fraction of component i

GREEK LETTERS

β_i	proportional constant component i
P	density (kg m^{-3})
ρ^*	maximum density of mixture (kg m^{-3})
ρ_i^*	maximum density of component i (kg m^{-3})
Δ	membrane thickness (m)
Γ	overlap factor
ϕ	volume fraction
γ_i	activity coefficient of component i
ξ_{ip}	ratio of critical molar volume of jumping unit of component i
ξ_{i3}	friction coefficient
$\xi_{i,\text{eff}}$	effective tracer friction coefficient

SUBSCRIPTS AND SUPERSCRIPTS

1	Water
2	Ethanol
3	PDMS membrane
i, j	Component index
F	Feed
M	Membrane
P	Permeate

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