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A mass transfer model for pure alcoholic permeation through the PDMS membrane

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ABSTRACT

This work focuses on the modeling of mass transfer in the pure compound pervaporation through hydrophobic membranes. For this purpose, a mathematical predictive model was established based on the solution-diffusion mechanism. In the sorption step, the Flory–Huggins theory was applied to predict the amount of component absorbed into the membrane. In the diffusion step, the generalized Fick's law with a constant diffusion coefficient and a concentration/temperature-dependent diffusion coefficient was employed to describe the component diffusion across the polydimethylsiloxane (PDMS) membrane. The concentration/temperature-dependent diffusion coefficient was determined using Duda's free volume theory. In order to solve the resulting nonlinear transport equations, both finite difference (FD) and finite element (FE) methods were employed. The proposed model enables to predict the permeation flux as well as the concentration, temperature, and diffusion coefficient profiles inside the membrane. The model was then validated using the experimental data obtained from the pervaporative process of pure substance with the PDMS membrane. The results showed that although both FD and FE approaches were able to solve the dominant equations with appropriate accuracy. The modeling case II was capable of predicting the permeation flux for systems of pure ethanol and isobutanol, respectively. Finally, the effect of feed temperature on the permeation flux was investigated.

Keywords: Pervaporation; Mass transfer modeling; Finite element; Free volume theory; Solution-diffusion mechanism

1. Introduction

Pervaporation is a membrane process in which a liquid mixture is separated due to its partial vaporization by passing through a nonporous membrane. During these years, pervaporation has been become a potential process to replace the conventional separating methods, such as solvent extraction and distillation, because of its operational benefits. The advantages of pervaporation process are as follows: moderate operating temperatures, there is no need to

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include additional chemicals and regeneration, and easy installation [1,2]. Understanding mass transfer through the selective layer of the membrane is fundamental for success in the development of new membrane materials and the improvement of the process designs. Several models suggested by different authors, such as resistance series model [3,4], computational fluid dynamics [5,6], or molecular dynamic simulation [7], to describe the transport phenomena in pervaporation process. Among the proposed models, the solution-diffusion model is most widely used in describing the mass transport through the pervaporation including sorption and diffusion steps. Shieh and Huang [8] assumed that the pervaporation process of a pure component is a combination of a liquid permeation mechanism and vapor permeation mechanism, and then, by thermodynamic equilibrium assumption, they could locate the interface between two mechanisms. Shah et al. [9] implemented computer simulations for transient permeation during the pervaporation process based on the solution-diffusion mechanism. Sumesh and Bhattacharya [10] utilized the solution-diffusion mechanism with the free volume theory to locate the region of phase change for pure methanol feed with the polydimethylsiloxane (PDMS) membranes in the pervaporation process. Also, Huang et al. [11] applied the modified solution-diffusion method with the free volume theory to predict the separation performance of alkane/2-methylthiophene and alkane/thiophene mixtures using the PDMS membrane. Furthermore, Raisi et al. [12] proposed a predictive mass transfer model using the Maxwell–Stefan with the free volume theory for the pervaporation process in order to recover aroma compounds from aqueous solutions based on the solution-diffusion mechanism. In addition, finite differences (FD) and finite element (FE) methods are two well-known mathematical approaches for solving the transport equations. For example, McCallum and Meares [13] as well as Mulder and Smolder [14] used the FD method to solve the mass transport equations of the binary pervaporation. Lipnizki and Field [15] employed a FE in the succession method to simulate the recovery of organic compounds from wastewater by using a plate and frame module. Also, Villaluenga and Cohen [16] proposed a numerical model of non-isothermal pervaporation. The model consisted of the coupled Navier-Stokes equations, the energy equation and the species convection–diffusion equations. The coupled nonlinear transport equations were solved simultaneously for the velocity, temperature, and concentration fields via a FE approach. Staniszewski and Kujawski [17] used the FD method to calculate the concentration profile of permeants inside the membrane based on the solution-diffusion theory.

The main goal of this study is to develop a mass transfer model based on the solution-diffusion theory to predict the permeation flux and concentration profile of the permeant inside the membrane. Moreover, the temperature profile inside the membrane is also calculated which can hardly be seen in the literature. For this purpose, three cases are considered: (I) the component diffusion coefficient is constant, (II) the diffusion coefficient depends on the component concentration inside the membrane, and (III) the diffusion coefficient depends on the component concentration and temperature inside the membrane. The mass transfer model is validated by the experimental data from the pervaporation of the pure ethanol liquids through a commercial composite PDMS membrane. In this paper, the FE and FD methods are used to solve the transport equations, and finally, their results are compared with each other to determine which method offers a better solution.

2. Mass transfer model development

The solution-diffusion model is the accepted mechanism for describing the permeation in the polymeric membranes [18]. The solution-diffusion method includes two major steps: first sorption and then diffusion of components across the membrane. The appropriate assumptions made in the present work are presented below:

(1) The temperature across the membrane thickness is constant except for case III. (2) The permeation of the components through the membrane is considered one dimensional and steady state. (3) There is no chemical reaction through the membrane. (4) The resistance of the feed side boundary layer and the microporous support of the membrane for transport of the penetrants are negligible. According to the resistance-in-series model, mass transport in pervaporation is generally controlled by the resistance of components in the membrane active layer and transport resistance in the support layer is low and negligible [19,20]. (5) The permeate side of the membrane is dry for pervaporation under the permeate pressure of 1 mm Hg.

2.1. Sorption into the membrane

There is a reasonable assumption that the thermodynamic equilibrium occurs at the feed and polymeric membrane interface, and therefore, the thermodynamic interaction between pure component and

PDMS determines the amount of substance sorption into the membrane. Several thermodynamic models have been proposed to predict the level of sorption and thermodynamic interaction [21]. Due to the mathematical simplicity, the Flory–Huggins theory has been applied in many studies. Mulder and Smolder [14] successfully utilized the Flory–Huggins thermodynamic to predict the concentration profiles and sorption behavior of cellulose acetate membranes for ethanol/water mixtures. Thiyagarajan et al. [22] used this theory to describe the separation of methylethyl ketone/water mixtures by the PDMS membrane. Also, Raisi et al. [12] applied the same theory for describing the sorption of aroma compounds from their aqueous solutions into the PDMS membranes. Furthermore, Mafi et al. [23] employed Flory–Huggins theory to estimate the sorption behavior of ethanol/water mixture in PDMS membrane. The activity of pure component in the binary system with polymeric solution can be described by the Flory–Huggins thermodynamics using the following equation [24]:

$$\ln a_1 = \ln \varphi_1 + \left(1 - \frac{V_1}{V_{\mathrm{p}}}\right)\varphi_{\mathrm{p}} + \chi_{1\mathrm{p}}\varphi_{\mathrm{p}}^2 \tag{1}$$

where φ and V are the volume fraction and molar volume, respectively, and index i and p represent pure component and PDMS membrane, respectively. χ_{ip} is the solvent/polymer interaction parameter.

2.2. Diffusion through the membrane

Fig. 1 shows the domain of the model. By considering the model assumptions, the differential form of continuity equation for the alcohols is simplified to:

$$\frac{\partial J_1}{\partial x} = 0 \tag{2}$$

Based on Lee's equation for a flat membrane at steady-state conditions, the flux of penetrants can be expressed as the following equation [25]:

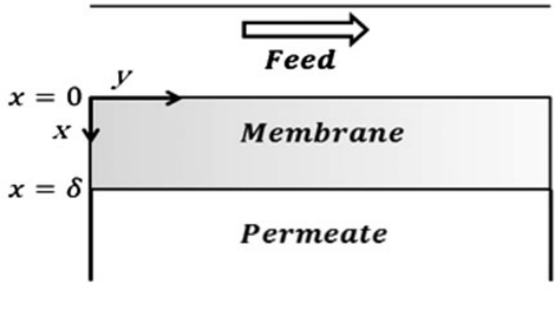

Fig. 1. Model domain of flat membrane module.

$$J_1 = -\frac{D_1 \rho_1 \varphi_1}{\mathrm{RT}} \frac{d\mu_1}{dx} \tag{3}$$

Under isothermal conditions, the pressure and concentration contribute to the chemical potential. Since the pressure difference between the feed side and permeate side is about 1 bar, the contribution of the pressure gradient in respect to the activity gradient can be neglected, and therefore, Eq. (3) is rearranged as:

$$J_1 = -D_1 \rho_1 \varphi_1 \left(\frac{d \ln a_1}{dx}\right) \tag{4}$$

The activity is determined from the Flory–Huggins theory for a binary system [24]. Therefore, Eq. (4) can be written as follow by applying Flory–Huggins theory:

$$\rho_1 \frac{d}{dx}\left[\varphi_1 D_1 \left(\frac{\partial \ln a_1}{\partial \varphi_1} \frac{d\varphi_1}{dx}\right)\right] = 0 \tag{5}$$

The above equation will be solved for three distinctive cases: (I) the diffusion coefficient for pure substance inside the membrane is independent of the species concentration and temperature, (II) the diffusion coefficient is dependent on the species concentration but independent of temperature, and (III) the diffusion coefficient is dependent on the species concentration and temperature.

In the latter case, the energy equation should be solved for the membrane region. Based on the proposed assumptions, the energy equation for a binary system is simplified to:

$$\lambda_{\mathrm{p}} \frac{\partial^2 T}{\partial x^2} + \frac{LJ_1}{\delta} = 0 \tag{6}$$

2.3. Free volume theory

The voids and intermolecular spacing between the polymer chains cause the diffusion of pure alcohol molecules to occur. A number of models have been developed using free volume theory for prediction of the penetrant diffusion coefficient through the membrane. For example, Wesslingh's free volume theory was applied by Raisi et al. [12] to predict the aroma compounds diffusion coefficients through the PDMS membrane. Sumesh and Bhattacharya [10] utilized Duda's free volume theory to locate the region of phase change for pure methanol feed with the PDMS membranes. Yeom and Huang [26] applied 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 its aqueous solution through the PDMS membrane. Furthermore, Mafi et al. [23] applied Duda's free volume theory to describe the diffusion behavior of water/ethanol mixture through the PDMS membrane. It is often acceptable to neglect the critical energy which a molecule possesses to overcome the attractive forces holding it to its neighbors in order to predict diffusion behavior [28]. Based on Duda's free volume theory [28,29] for a binary system, the penetrant/membrane diffusion coefficient is given by:

$$D_1 = D_0(T)\exp\left(-\frac{w_1\hat{V}_1^* + \xi_{1p}W_p\hat{V}_p^*}{\frac{\hat{V}^{FH}}{\Gamma}}\right)(1-\varphi_1)^2(1-2\chi_{1p}\varphi_1) \quad (7)$$

$$\hat{V}^{FH}/\Gamma = w_1\frac{k_{I,1}}{\Gamma}(k_{II,1} - T_{g,1} + T_f) + w_p\frac{k_{I,p}}{\Gamma}(k_{II,p} - T_{g,p} + T_f) \quad (8)$$

where D_0 is the zero concentration diffusion coefficient of penetrant through the membrane in binary system which is determined by the Wilke–Chang theory [30]. The required parameters of Eqs. (7) and (8) for some solvents and polymers can be found in the literatures [28,29]. The required free volume parameters for isobutanol are determined based on its viscosity data [28,29]. The free volume parameters for the systems of current study are presented in Table 1.

3. Experimental

The pervaporation experiments were conducted for pure ethanol (99.8%, Merck, Darmstadt, Germany) using a PDMS/PVDF/PP composite membrane with active layer thickness of 10 μm and for pure isobutanol (99.5%, Darmstadt, Germany) using a PDMS/PAN/PET composite membrane with active layer thickness of 6.1 μm. applied membrane were kindly provided by Helmholtz-Zentrum Geesthacht Zentrum fur Material und Küstenforschung GmbH, Geesthacht, Germany.

Table 1
Free volume parameters for the PDMS, ethanol, and isobutanol system

Parameters	Ethanol [20]	Isobutanol	PDMS [28,29]
$\hat{V}^*(\mathrm{cm}^3/\mathrm{g})$	0.987	1.004	0.905
$\frac{k_1}{\Gamma}\left(\frac{\mathrm{cm}^3}{\mathrm{gk}}\right)$	3.12×10^{-4}	1.42×10^{-3}	9.32×10^{-4}
$k_{II} - T_g(\mathrm{k})$	111.80	−150.41	−81.00
ξ_{ip}	0.545	0.893	–

The pervaporation apparatus has been previously described [31]. To determine the amount of pure component absorbed in the PDMS layer of the composite membrane, swelling measurements of the membranes were performed using a well-known gravimetric procedure as presented by Raisi et al. [20]. The ethanol sorption experiments were performed for the feed temperatures of 30, 35, 40, 45, 50, 55, and 60°C. Also the experiments for isobutanol were carried out for different temperatures of 30, 40, and 60°C. The results were reported as the ratio of the liquid weight uptake in membrane per gram of dry membrane as follows:

$$W^s = \frac{W_s - W_d}{W_s} \quad (9)$$

In this work, the effects of feed temperature on the permeation flux at the permeate-side pressure of 1 mm Hg were determined. All experimental conditions were repeated three times, and the average values are reported. Steady-state permeation was reached at the second hour in all experimental conditions. The time duration of each experiment was 8 h, and a permeate sample was collected every one hour.

4. Method of solution

The proposed mass transfer model enables to predict the penetrant flux based on the Flory–Huggins, Duda's free volume and Lee's permeation theories without the need of any adjustable parameters. For the prediction, only a number of physical properties of the components, PDMS membrane and the sorption equilibrium of pure components in the PDMS membrane are required. The following procedures are used to solve the model.

By considering an assumption that there is thermodynamic phase equilibrium between the feed solution and the membrane, the chemical potential of ethanol is equal in both phases. Based on this assumption, the volume fraction of pure substance is determined at the membrane/feed interface from experimental data. The chemical potential equality can be expressed as an equality of the activities:

$$a_1^{f} = a_1^{m} \quad (10)$$

As the activity of pure component is equal to unity, therefore, Eq. (1) is simplified to the following equation in which the solvent/polymer interaction parameter (χ_{ip}) can be calculated [24]:

$$\chi_{1p} = -\frac{\ln(1-\varphi_p) + \varphi_p}{\varphi_p^2} \quad (11)$$

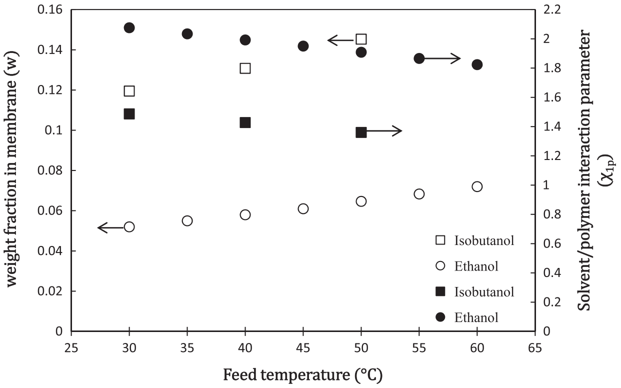

Fig. 2. Absorbed weight fraction of pure alcohol and solvent polymer interaction parameter for both ethanol and isobutanol.

Here, φ_p is obtained from the experiments of pure liquid components sorption in the PDMS membrane. The experimental pure component weight fraction in PDMS membrane and the calculated values of (χ_{1p}) are represented in Fig. 2.

It is assumed that the permeate side of the membrane is dry for the pervaporation under high vacuum, and therefore, the volume fraction of component at the membrane/permeate is equal to zero. At the membrane/feed interface, the membrane is continuously in contact with the feed solution and the membrane has enough time to reach to the feed temperature, in other words, the system of feed/membrane at the feed-side is in thermal equilibrium:

$$\text{at } x = 0; T = T^f \tag{12}$$

There is a region inside the membrane where phase change of the penetrants occurs. After this point, it is reasonably acceptable that the temperature of system has no significant change. The boundary condition at the permeate-side of the membrane can be concluded as follows:

$$\text{at } x = \delta; \quad \frac{\partial T}{\partial x} = 0 \tag{13}$$

The FD method and the weak form Galerkin FE method are used to solve the coupled nonlinear equations to determine the component partial fluxes as well as the concentration and temperature profiles through the membrane. All mathematical computer programs are run by using a commercial SONY VAIO laptop vpcs116FG.

5. Results and discussion

5.1. Comparison between FE and FD methods

For a comparison between two methods of solution and the experimental results, an error is assessed by applying the average absolute relative deviation (AARD) which is defined as follows:

$$\text{AARD\%} = \frac{1}{n_{\text{exp}}} \frac{|J_{\text{expi}} - J_{\text{cali}}|}{J_{\text{expi}}} \times 100 \tag{14}$$

where J_{expi} and J_{cali} are the experimental and calculated value of the pure substance flux, respectively, n_{exp} is the number of experimental points. In addition, the average run time that is defined as the time takes for the solution methods to reach their stable results approximately. The results are reported in Table 2 for the specific number mesh grids ($N = 2000$ for FD method and $N = 250$ for FE method). Albeit the FD method has slightly better precision than the FE method, its average run time is significantly much higher than the FE method. Also, by increasing the mesh grids for the FD method, the predicted results become closer to the FE results. As can be seen from Table 2, there is no significant difference between case II and III with both methods of solution. Moreover, the predicted results of case II and III are relatively in good agreement with the experimental results which indicate that the concentration dependency of the components diffusion coefficient inside the membrane

Table 2
The results of two different methods of solution

	AARD (%)				Average run time (S)			
	FD		FE		FD		FE	
	Ethanol	Isobutanol	Ethanol	Isobutanol	Ethanol	Isobutanol	Ethanol	Isobutanol
Case I	42.45	69.57	42.67	69.07	418	412	4	4
Case II	9.09	25.38	9.10	25.44	1,673	1,471	5	5
Case III	9.08	25.38	9.11	25.44	5,132	4,878	78	85

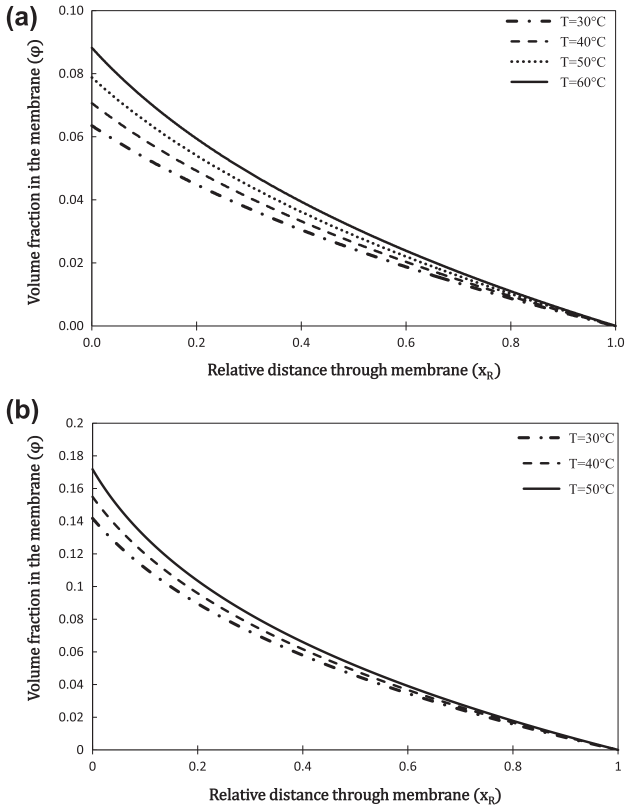

Fig. 3. Pure substance concentration profiles through the PDMS membrane for different feed temperatures by using modeling case II: (a) ethanol, (b) isobutanol.

must be taken into account. As a result, in the following sections, the results acquired by using FE are presented.

5.2. Concentration and temperature profiles

The concentration profile inside the PDMS membrane for pervaporative separation of pure component liquid at different feed temperatures has been calculated in three modeling cases. The results are presented in Fig. 3. As can been seen from this figure, when the feed temperature increases, the amount of pure alcohol absorbed in the membrane increases and this leads to higher permeation flux. In addition, at the same feed temperature, the amount of sorption of isobutanol is greater than that of ethanol in PDMS membrane. Since PDMS membrane is hydrophobic and nonpolar, it inclines to absorb the material which has pretty the similar characteristics. Isobutanol has the longer carbon chains which facilitate the sorption of isobutanol in the PDMS because the carbon chains conquer to opposite effects of hydroxyl groups. While ethanol has predominant hydroxyl group in comparison with its carbon chains, ethanol hydroxyl group resists being absorbed in PDMS membrane, and therefore, PDMS membrane absorbs isobutanol more conveniently.

Besides, the temperature profile inside the membrane has been obtained only for case III. The results are shown in Fig. 4. It is observed that the temperature would not vary significantly through the membrane for both systems, thus, considering a constant temperature inside the membrane is a reasonable assumption for the mass transfer modeling.

5.3. Diffusion coefficient profiles

Ethanol and isobutanol diffusion coefficients through the membrane by applying Duda's free volume theory have been computed. The results are shown in Fig. 5. As can be seen from Fig. 5, the enhancement in feed temperature contributes to increase the diffusion coefficients. Since the proposed mass transfer model is directly proportional to the diffusion coefficient, this enhancement leads to pure component flux boost; moreover, at the same feed

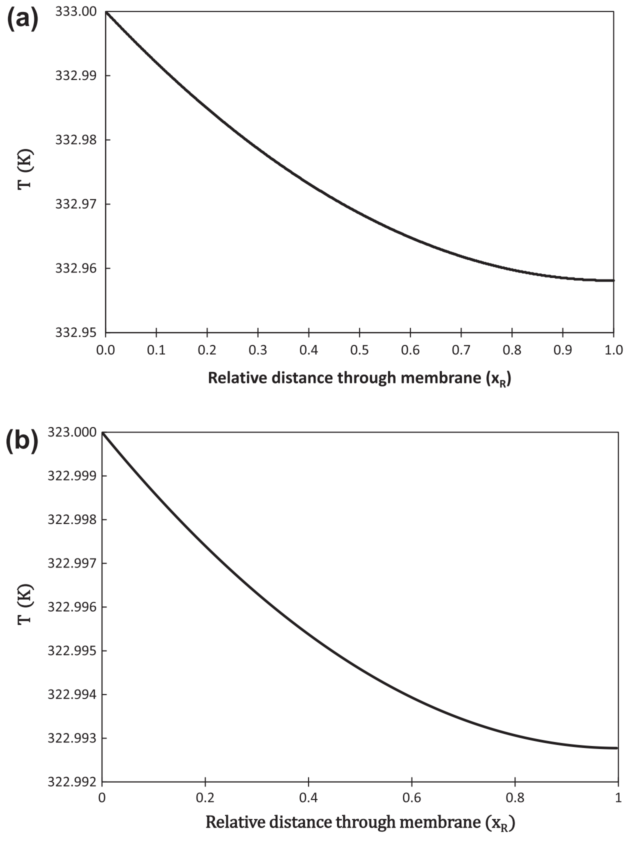

Fig. 4. The temperature profile through the PDMS membrane at by using modeling case III: (a) ethanol feed temperature of 60°C, (b) isobutanol feed temperature of 50°C.

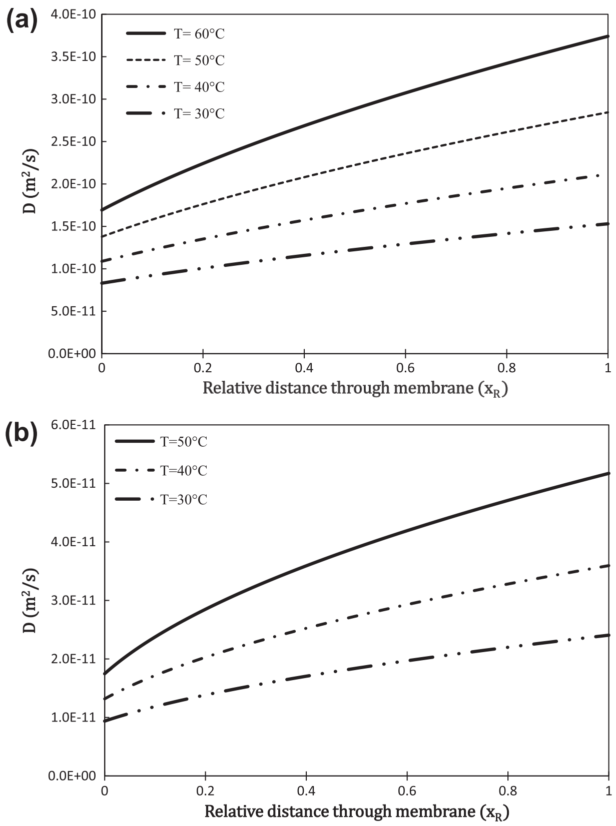

Fig. 5. Pure substance diffusion coefficient profiles through the PDMS membrane for different feed temperatures by using modeling case II: (a) ethanol, (b) isobutanol.

temperature, the diffusion coefficient of ethanol compared to that of isobutanol is greater. As the free volume between polymer chains is the only possible path for the diffusion of molecules in the PDMS membrane, the behavior could be relevant to molecular size. Ravdel et al. [32] mentioned that the molecule size of ethanol and isobutanol is 4.46 and 7.7 Å, respectively. Thus, the ethanol molecules diffuse across the matrix membrane easier than the isobutanol molecules do due to smaller molecule sizes.

5.4. Effect of feed temperature on permeation flux

Feed temperature has a very important role in the pervaporation due to its influence on the solubility and the diffusion of the components in the membrane. The effect of feed temperature on the pure flux is presented in Figs. 6–8. As can be seen from these figures, the pure alcohol flux enhances when the feed temperature increases. Three modeling cases could predict this trend successfully. To illustrate, the modeling case I predicted that the isobutanol flux enhanced from 0.471 to $0.536\,\mathrm{kg/m^2\,h}$ when the feed temperature increased from 30 to 50℃. According to the free volume theory in a polymeric membrane, the

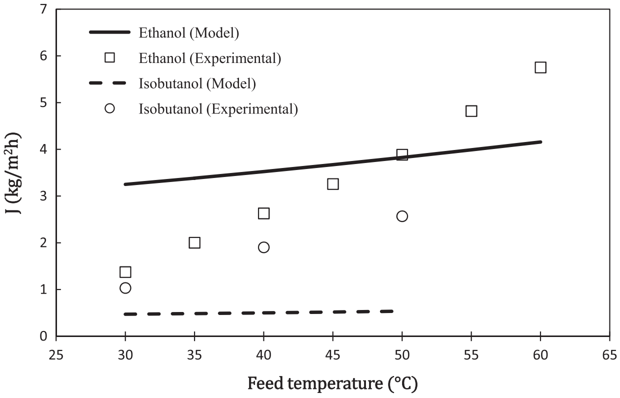

Fig. 6. The effect of feed temperature on the pure component flux by using modeling case I.

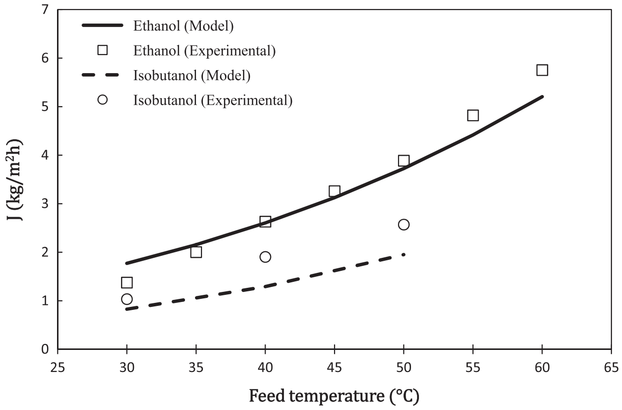

Fig. 7. The effect of feed temperature on the pure component flux by using modeling case II.

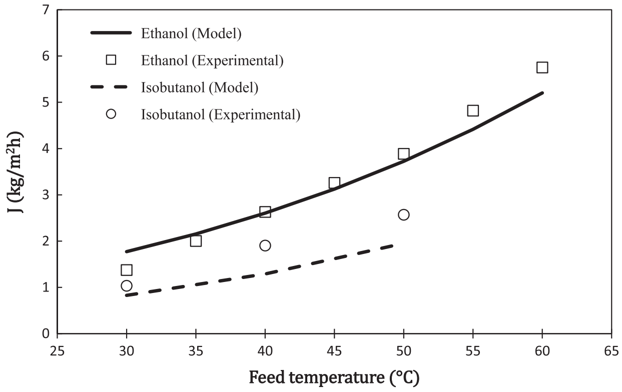

Fig. 8. The effect of feed temperature on the pure component flux by using modeling case III.

penetrant can diffuse through the free volumes of the membrane. The free volume in the polymeric membrane can be made from segmental motions of the polymer chain in the amorphous regions. When the feed temperature increases, a segmental motion in the membrane polymer chain will be increased. As a result, the free volume in the membrane goes to a higher degree, and thus the diffusion rate of the individual permeating molecules increases, leading to a high permeation flux as the temperature increases. Furthermore, as the equilibrium vapor pressure of the permeating molecules varies with temperature, the feed temperature influences the driving force of the process. An increase in the equilibrium vapor pressure of the pure component due to the increase of feed temperature results in high permeation flux.

As observed from Figs. 6–8, the predicted results of modeling case II and III are in good agreement with the experimental results, while no significant difference can be seen between models of case II and III. Furthermore, it is observed that these models have better prediction than modeling case I. This indicates that the penetrant diffusion coefficient dependencies on the components concentration must be taken into account.

6. Conclusions

Mass transfer in the pervaporation process of pure liquids through a PDMS membrane was investigated by a predictive mass transfer model based on the solution-diffusion theory. The concentration, temperature, and diffusion coefficient profiles as well as the permeation flux through the membrane were predicted via three different modeling cases by using two different mathematical solutions. By modeling case II and III, the results showed that the predicted flux were in good agreement with the experimental observations. The modeling case II was capable of predicting the permeation flux with 9 and 25% AARD for systems of pure ethanol and isobutanol, respectively. Also, there is no significant difference between the predicted amount of case II and III, therefore considering the temperature as constant through the membrane during computation is reasonable. Two numerical methods could solve the transport equations successfully. While there is no significant difference in the accuracy of both solution methods, the FE method is preferable because of its much shorter run time. Moreover, the results indicated that as feed temperature increased, the predicted and experimental permeation fluxes enhanced. Finally, it can be concluded that the permeation fluxes are satisfactorily predicted with the proposed model without the need for any adjustable parameters and the model enables to predict the feed temperature effect on the performance of hydrophobic pervaporation for the pure substances.

Acknowledgments

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Nomenclature

a_1 — activity of ethanol
D_1 — diffusion coefficient of ethanol into the membrane (m^2/s)
D_0 — zero concentration diffusion coefficient of ethanol (m^2/s)
J — mass flux of component (kg/m^2s)
$k_{I,i}$ — free volume parameter of component i ($cm^3/g.K$)
$k_{II,i} - T_{g,i}$ — free volume parameter of component i (K)
L — latent heat of vaporization (kJ/kg)
R — gas constant (8.314 J/mol.K)
T — absolute temperature (K)
V — molar volume (m^3/mol)
$\hat{V}_{i^*}$ — specific hole free volume of component i (cm^3/g)
$\hat{V}_i^{FH}$ — average hole free volume per gram of component i (cm^3/g)
W_d — weight of dry membrane (g)
W_s — weight of swollen membrane (g)
w_i — weight fraction of component i
w^s — weight fraction of component i in the swollen membrane
x — penetration direction (m)
x_R — relative distance through membrane ($x_R = \frac{x}{\delta}$)

Greek letters

ρ — density (kg/m^3)
λ — heat conductivity (J/m.s.℃)
δ — membrane thickness (m)
Γ — overlap factor
χ_{ip} — polymer/solvent interaction parameter
φ — volume fraction
ε_{ip} — ratio of critical molar volume of jumping unit of component i

Subscripts and superscripts

1 — ethanol
f — feed
m — membrane
p — PDMS membrane

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