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Mathematical modelling of sorption and permeation through composite membrane in pervaporation process

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ABSTRACT

This study focuses on the contribution of the sorption models on the pervaporation modeling in order to predict the mass transfer through the membrane and the separation performance of the pervaporation process. For this purpose, application of three thermodynamic models, i.e. the UNIQUAC, Flory-Huggins and poly-NRTL, for modeling of the compounds sorption and permeation through the membrane in the pervaporation process was investigated. The finite element method was used to solve the governing transport equations. The proposed model enables to describe the effects of feed temperature and concentration on the partial fluxes and permeate concentration through the membrane as well as on the concentration profile inside the membrane. The results revealed that the applied thermodynamic models could successfully predict the amount of ethanol sorbed by the pure polydimethylsiloxane membrane and the sorption values obtained by the UNIQUAC equation were thoroughly agreement with the experimental data in all ethanol feed concentrations.

Keywords: Pervaporation; Mass transfer model; Sorption; UNIQAUC; Flory-Huggins; Poly-NRTL

1. Introduction

Pervaporation is a membrane process for the separation of liquid mixture by selective transport through a dense membrane combined with a phase change of the permeating components from liquid to vapor. So far, several models have been proposed to describe the mass transport through the membrane in the pervaporation process [1], among them the solution-diffusion model is most widely used [2]. This model describes the mass transfer of permeants through the membrane in three consecutive steps: i) selective sorption of components into the membrane at the feed side of the membrane, ii) selective diffusion of components through the membrane and iii) desorption of components into a vapor phase at the permeate side of the membrane.

The sorption and diffusion are the most important steps in the pervaporation which determine the permeation flux and selectivity of the process. The thermodynamic interactions between the permeating components and the membrane directly determine the level of sorption and indirectly affect the diffusion of penetrants across the membrane thickness. Therefore, utilizing appropriate thermodynamic model regarding the chemical and physical nature of the system is necessary to describe the mass transfer in the both steps. Several thermodynamic models have been applied in earlier investigations as reviewed by [3]. However, the predictive models that are no adjustable parameters are preferred. For example, Mulder and Smolders [4] employed the Flory-Huggins theory to determine the activities of water and ethanol in homogeneous cellulose acetate membranes. Favre et al. [5,6] used the Flory-Huggins theory with constant interaction parameters for prediction of equilibrium volume fractions of liquid mixtures in a polymer network.

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They observed that the Flory-Huggins theory offers reasonable prediction in the case of apolar liquids in an elastomeric polymer. Liu et al. [7] developed a transport model for penetrants in glassy polymer membrane by combining the Flory–Huggins theory with the mass conservation equation and phenomenological diffusive flux expression. Hoda et al. [8] employed the Flory–Huggins model to determine the solubility of hydrazine/water into the ethyl-cellulose membrane. Han et al. [9] also applied the Flory-Huggins theory in combination with Fick's law to calculate the permeation fluxes of isopropanol/water mixtures through poly (vinyl alcohol) (PVA) membrane. Moreover, various modifications have been performed on the Flory-Huggins theory in order to model the sorption of permeating compounds in the glassy [7], swollen [10] and semi-crystalline [11] polymers.

The group-contribution methods like UNIFAC and modified UNIFAC models have also been used for prediction of sorption into the polymeric membranes. Peng et al. [12] applied the UNIFAC model for the dilute benzene aqueous solutions in the feed phase and the UNIFAC-FV for predicting the solubility of penetrant components inside the polydimethylsiloxane (PDMS) membrane. They also combined their proposed model with Fujita free volume theory to determine the effects of feed aroma concentration and temperature on the pervaporation performance. Bettens et al. [13] coupled the UNIFAC model with the Maxwell–Stefan equations to model the pervaporation of binary water/alcohols and methanol/alcohols mixtures through the methylated microporoussilica membranes.Raisi et al. [14] and Mafi et al. [15] applied the Flory-Huggins model in combination of the UNIFAC model for prediction the sorption and permeation of aroma compounds and ethanol in the PDMS membranes, respectively. Kuila and Ray [16] described the coupling in sorption by activity coefficient of water and isopropyl alcohol in the feed and membrane using Flory-Hugging thermodynamics and also by Engaged species induced clustering (ENSIC) model.

The UNIQUAC model [17–20] and their extended ones [21,22] are other thermodynamic models which have been successfully employed for the modeling of membrane processes. Enneking et al. [18] as well as Heintz and Stephan [17] determined the solubility values and permeation flux of multicomponent mixtures in the pervaporation with hydrophilic and hydrophobic membranes, respectively. The UNIQUAC-HB that developed to account for strong interactions by hydrogen bonding, was used by Heintz and Stephan [17]for the modeling the sorption of aqueous/organic mixtures in the PVA membrane. Yang and Lue [22] employed the UNIQUAC, UNIQUAC-HB and Flory-Huggins models to predict the sorption levels from various ethanol-water mixtures into the PDMS. They reported that the UNIQUAC-HB model is advantageous over the UNIQUAC and Flory–Huggins model because the UNIQUAC-HB model is able to predict the synergistic effect of ethanol on the solubility of water. The UNIQUAC-FV model which extended to account for free volume effects and the UNIQUAC-FV-HB model were applied by Jonquieres et al. [21] for modeling the sorption phenomena of ether, ester and alcohol in polyurethaneimides (PUI) membranes. They observed that the UNIQUAC-FV provides the best prediction for the sorption of ether and ester in the PUI membranes. Moreover, other thermodynamic models such as ASOG-FV[23], NRTL [1], modified NRTL [24] and Entropic-FV [25] have been used to investigate the solubility of components in the polymers.

In the previous studies [15,26], we investigated the contribution of the models used for the diffusion step on the mass transport modeling of the pervaporation process and it was found that the penetrant diffusion coefficient dependencies on the component concentrations must be taken into account and it is reasonable to ignore the temperature variation through the membrane. Recently, we employed the Gibbs free energy models such as the modified NRTL and modified Wilson for modeling the sorption step in the pervaporation of the ethanol/water mixtures into the PDMS membranes [27]. A search in the literature reveals that there are only a few researches on the contribution of the sorption models on the pervaporation modeling in order to predict the mass transfer through the membrane and the separation performance of the pervaporation process. The aim of this work is to develop a mathematical model for the hydrophobic pervaporation process based on the solution-diffusion theory using a thermodynamic model, generalized Fick's law and free volume theory. Three thermodynamic models, the UNIQUAC, Flory-Huggins and modified NRTL models are used to calculate the equilibrium activities of permeating components in both feed and membrane phases, and the relative performance of these models to determine the sorption and permeation of components through the PDMS membrane is investigated. The finite element method is employed to solve the mass transfer equations to obtain the partial fluxes and permeate concentration. Besides, the ability of the proposed model for prediction the influences of two key operational parameters such as feed ethanol concentration and feed temperature on the pervaporation performance are investigated. Finally, the model is validated by experimental data from the pervaporation of ethanol/water binary solutions through a commercial composite PDMS membrane.

2. Mass transfer modeling

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. (iv) The permeate side of the membrane is dry for pervaporation under permeate pressure of 1 mm Hg.

Based on the solution-diffusion mechanism, the sorption and diffusion of components through the membrane are the most important steps in the pervaporation process by determining the mass transfer rate of components and the membrane selectivity. In the following section, the theoretical backgrounds of the model used in the sorption and diffusion steps are explained.

2.1.Sorption into the membrane

It is assumed that the equilibrium state is reached at the interface between the feed and the polymeric membrane phases. Therefore, the thermodynamic interactions between the penetrants and polymer dictate the level of sorption. In the following, three different thermodynamic models such as the UNIQUAC, the Flory-Huggins and the poly-NRTL models which will be used for modeling the sorption step are briefly explained. Furthermore, the method of adjusting the required parameters and calculating the equilibrium concentration is described.

2.1.1. The UNIQUAC model

The UNIQUAC model is established to describe the excess Gibbs free energy of a mixture as a function of composition and temperature [28]. This activity model is able to express the polymer solution with the high precision [17,19,21]. According to the UNIQUAC equation, the activities of components are affected by combinatorial (a_i^C) and residual (a_i^R) contributions regarding the difference in molecular size and energy [28,29]:

$$\ln a_i^C = \ln \varphi_i + \left(\frac{Z}{2}\right) q_i \ln \frac{\theta_i}{\varphi_i} + l_i - \frac{\varphi_i}{x_i}\left(\sum_{j=1}^{N} x_j l_j\right) \tag{1}$$

$$\ln a_i^R = q_i - q_i \ln\left(\sum_{j=1}^{N} \theta_j \tau_{ji}\right) - q_i \left[\sum_{j=1}^{N} \frac{\theta_j \tau_{ij}}{\sum_{k=1}^{N} \theta_k \tau_{kj}}\right] \tag{2}$$

$$l_i = \frac{Z}{2}\left(r_i - q_i\right) - \left(r_i - 1\right) \tag{3}$$

where x_i, θ_i and φ_i are the mole, volume and surface fractions of component *i*, respectively. *Z* is a coordination number that is considered to be 10. *N* is the number of components in mixture. r_i and q_i are the molecular Van der Waals volume and surface area of component *i*, respectively.

The UNIQUAC binary interaction energy parameter (τ_{ij}) which represents the characteristics for either solvent–polymer or solvent–solvent molecules and needs to be adjusted for the proposed model. In present study, this interaction parameter was assumed as a linear function of temperature:

$$\tau_{ij} = \exp\left(-\frac{a_{ij} + b_{ij}T}{RT}\right) \tag{4}$$

2.1.2. The Flory-Huggins model

The Flory-Huggins model is one of the interesting approaches applied in the sorption modeling because of its mathematical simplicity. In the feed phase, activity of component *i* is determined by the extended Flory-Huggins equation [30]:

$$\ln a_i = \ln \varphi_i + \chi_{ij} \varphi_j^2 + \left(1 - \frac{V_i}{V_j}\right) \varphi_j + \varphi_i \varphi_j^2 \frac{\partial \chi_{ij}}{\partial \varphi_i};\ i = 1,2; i \neq j \tag{5}$$

For the membrane phase, the penetrant activities inside the membrane are obtained as follows:

$$\begin{aligned}\ln a_1 = {} & \ln \varphi_1 + \left(1 - \varphi_1\right) - \varphi_2 \frac{V_1}{V_2} - \varphi_3 \frac{V_1}{V_3} + \left(\chi_{12}\varphi_2 + \chi_{13}\varphi_3\right)\left(\varphi_2 + \varphi_3\right) \\ & - \chi_{23} \frac{V_1}{V_2} \varphi_2 \varphi_3 - u_1 u_2 \varphi_2 \frac{\partial \chi_{12}}{\partial u_2}\end{aligned} \tag{6}$$

$$\begin{aligned}\ln a_2 = {} & \ln \varphi_2 + \left(1 - \varphi_2\right) - \varphi_1 \frac{V_2}{V_1} - \varphi_3 \frac{V_2}{V_3} + \left(\chi_{12}\varphi_1 \frac{V_2}{V_1} + \chi_{23}\varphi_3\right)\left(\varphi_1 + \varphi_3\right) \\ & - \chi_{13} \frac{V_2}{V_1} \varphi_1 \varphi_3 + \frac{V_2}{V_1} u_1^2 \varphi_2 \frac{\partial \chi_{12}}{\partial u_2}\end{aligned} \tag{7}$$

where φ and *V* are the volume fraction and molar volume, respectively and index 1, 2 and 3 refer to water, ethanol and PDMS membrane, respectively. u_1 is the water volume fraction in the ethanol/water mixtures in the polymer and u_2 is the ethanol volume fraction in the ethanol/water mixtures in the polymer. Two types of interaction parameters are used in Eqs. (5)–(7) solvent/polymer interaction parameters (χ_{13},χ_{23}) and solvent/solvent interaction parameter (χ_{12}). It should be noted that the χ_{12} is considered as a function of volume fractions of water and ethanol [15]:

$$\chi_{12} = a\ \exp\left(b u_2\right) \tag{8}$$

2.1.3. The poly-NRTL model

Sadeghi and Zafarani-Moattar [31] extended the NRTL model to predict the behavior of polymer-polymer aqueous two-phase systems. The results indicated that the extended NRTL model can be predicted the phase behavior of polymer solutions in good agreement with the experimental data. They proposed the modified NRTL model considering entropic contribution which is determined by the Flory-Huggins theory and the local composition concept. The activity of each species in binary solutions is calculated as [31]:

$$\begin{aligned}\ln a_i = {} & \ln\left(\varphi_i\right) + \sum_{j=1}^{N}\left(1 - \frac{V_i}{V_j}\right)\varphi_j \\ & + \sum_{i=1}^{N}\left[\frac{\sum_{j=1}^{N}\varphi_j G_{ji}\tau_{ji}}{\sum_{k=1}^{N}\varphi_k G_{ki}} + \sum_{j=1}^{N}\frac{\varphi_j G_{ij}}{\sum_{k=1}^{N}\varphi_k G_{kj}} \times \left(\tau_{ij} - \frac{\sum_{k=1}^{N}\varphi_k G_{kj}\tau_{kj}}{\sum_{k=1}^{N}\varphi_k G_{kj}}\right)\right]\end{aligned} \tag{9}$$

where τ_{ij} and G_{ji} are the NRTL parameters. G_{ji} is defined as follows:

$$G_{ij} = \exp\left(-\alpha_{ij}\tau_{ij}\right) \tag{10}$$

where α_{ij} is non-randomness factor and is equal to 0.2. For the poly-NRTL model, τ_{ij} needs to be adjusted and the following relation is chosen to express the temperature dependency of the NRTL interaction parameter:

$$\tau_{ij} = \frac{a_{ij} + b_{ij}T}{RT} \tag{11}$$

2.2. Calculation of equilibrium volume fraction

As can be referred from Fig. 1, there are two phases involving in the sorption step. With considering the assumption that thermodynamic equilibrium reach at the feed/membrane interface, the volume fraction of penetrants can be estimated. It can be inferred from the fundamental relations of thermodynamic the iso-activity criterion for each species must be confirmed as:

$$a_i^f = a_i^m \tag{12}$$

where a is the component activity and superscripts f and m stand for the feed and membrane, respectively.

The procedure of this work is to apply the same thermodynamic activity models for both phases since it provides enough generality for the proposed model. To estimate the volume fraction at the feed/membrane interface, it is required to obtaining the model parameters. For this purpose, the experimental weight fractions are converted to the volume fraction and then are used to set the required parameters. The following objective function is considered based on the thermodynamic equilibrium criterion between feed and membrane as:

$$\Omega = \frac{100}{N}\sum_{i=1}^{N}\frac{\left|a_i^f - a_i^m\right|}{a_i^f} \tag{13}$$

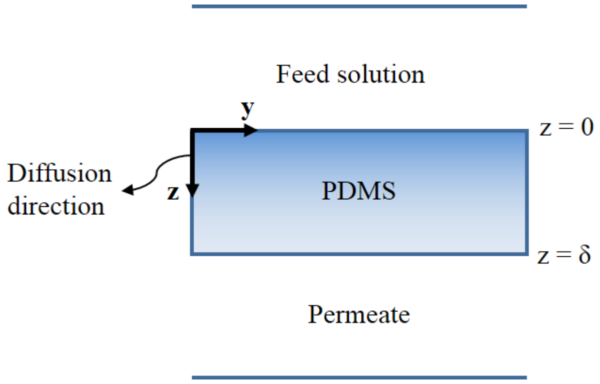

Fig. 1. The model domain of the flat membrane module.

Table 1
The required adjusted parameters for the Flory-Huggins model

T/°C	a	b	χ_{13}	χ_{23}
30	0.8124	–0.4813	3.5642	1.7046
45	0.8004	–0.6111	3.4178	1.5010
60	0.8262	–0.4752	3.2455	1.4439

Tables 1 and 2 represent the values of adjustable parameters for three different models. Once the adjustable parameters are estimated, the nonlinear equations (Eqs. (14) and (15)) must be solved simultaneously to find the equilibrium concentration for each experimental weight fraction:

$$\ln a_i^f - \ln a_i^m = 0 \tag{14}$$

$$\sum_{i=1}^{3}\varphi_i = 1 \tag{15}$$

The "*fsolve*" function of MATLAB software was used for the solving of Eqs. (14) and (15). The schematic diagram for estimation of the adjustable parameter and obtaining the volume fractions is indicated in Fig. 2.

2.3. Diffusion through the membrane

By applying the second assumption, the differential form of the continuity equation for each component through the membrane is simplified as follow:

$$\frac{\partial J_i}{\partial z} = 0 \tag{16}$$

where z and J_i are the direction of mass diffusion and component mass flux, respectively.

According to Lee's theory for a flat sheet membrane module in the stationary state, the flux of each component can be describe as the following equation [32]:

Table 2
The required adjusted parameters for the UNIQUAC and poly-NRTL models

	UNIQUAC			Poly-NRTL		
	T = 30°C	T = 45°C	T = 60°C	T = 30°C	T = 45°C	T = 60°C
a_{12}	–788.410	–807.482	–675.712	–257.651	–330.468	–310.616
b_{12}	0.5666	0.4033	–0.0140	0.04927	0.2796	0.1454
a_{13}	650.718	417.482	–3092.710	3270.830	3490.080	2670.690
b_{13}	1.169	3.137	46.527	4.629	4.557	8.354
a_{23}	1299.40	50230	62301.30	1294.32	1533.11	1231.59
b_{23}	1.0452	4.677	36.809	1.588	3.0852	7.688
a_{21}	–529.33	–688.68	415.85	–4118.42	–4267.17	–4500.47
b_{21}	6.009	6.703	3.075	20.792	20.624	20.900
a_{31}	–211.004	–226.198	323.180	504.316	546.319	462.184
b_{31}	0.8019	0.4485	–1.5598	–0.8219	–1.2237	–1.0826
a_{32}	–118.078	–312.032	117.739	677.998	664.523	509.659
b_{32}	1.437	1.763	0.110	3.610	3.1051	3.285

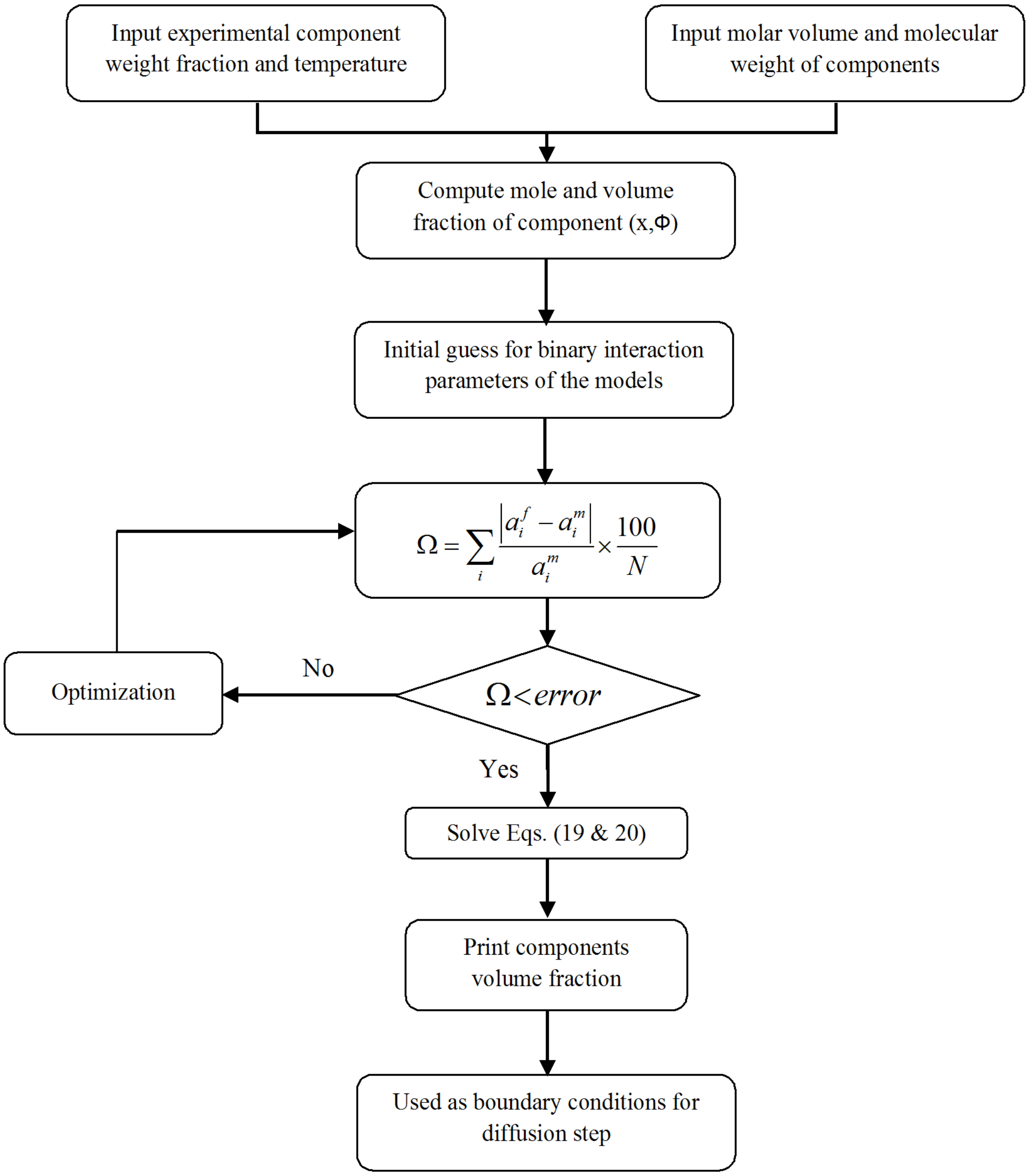

Fig. 2. The schematic diagram for estimation of the adjustable parameter and obtaining the volume fractions.

$$J_i = -\frac{\rho_i D_i \varphi_i}{RT}\frac{d\mu_i}{dz} \tag{17}$$

where ρ, μ and D are the density, chemical potential and diffusion coefficient for each component, respectively.

Under isothermal conditions, pressure and activity contribute to the chemical potential of component but the pressure gradient can be neglected in respect to activity because the pressure difference between feed phase and permeate phase in the pervaporation is about 1 bar, therefore, by taking this assumption into account Eq. (17) is rearranged to:

$$J_i = -D_i \rho_i \varphi_i \left(\frac{d\ln a_i}{dz}\right) \tag{18}$$

The penetrants activities are determined using one of the proposed thermodynamic models for the ternary system. When considering the coupling of fluxes, Eq. (18) can be rearranged as follow:

$$J_i = -\rho_i D_i \varphi_i \left(\sum_{j=1}^{2} \frac{\partial \ln a_i}{\partial \varphi_j}\frac{d\varphi_j}{dz}\right) \tag{19}$$

Therefore, by assuming that ρ_i is distance independent and substituting Eq. (19) in Eq. (16), the following differential equation can be derived:

$$\frac{d}{dz}\left[\varphi_i D_i \left(\sum_{j=1}^{2} \frac{\partial \ln a_i}{\partial \varphi_j}\frac{d\varphi_j}{dz}\right)\right] = 0 \tag{20}$$

For each species, two mass transfer boundary conditions are required. Furthermore, it is assumed that the permeate side of the membrane is dry for the pervaporation under high vacuum, and as a result, the volume fraction of components at the membrane/permeate is equal to zero. Hence, the following boundary conditions can be imposed for Eq. (18):

$$at\, z = 0;\ \varphi_i = \varphi_i^{eq} \tag{21}$$

$$at\, z = \delta;\ \varphi_i = 0 \tag{22}$$

Determining the diffusion coefficients for each species inside the membrane are perhaps the critical points for solving Eq. (20). For concentrated solutions, the diffusion coefficients of components through the membrane must be considered as a function of species concentration [15].The diffusion of molecules through the polymer networks basically occurs due to the passage of these molecules through the voids and intermolecular spacing between the polymer chains. In this study, Duda's free volume theory is used to predict the diffusion coefficients of penetrants through the PDMS membrane.

Finally, the differential equations (Eq. (20)) are solved numerically using the weak form Galerkin finite element method [33]. The basic steps which are performed to determine the component partial fluxes as well as the concentration profiles through the membrane were presented in the earlier study [15]. Finally, once the partial fluxes are determined, the weight fraction of aroma compounds in the permeate stream is calculated using the partial fluxes:

$$w_i^P = \frac{J_i}{\sum_{j=1}^{2} J_j} \tag{23}$$

To compare the predicted results with the experimental data, the error is assessed by applying the average absolute relative deviation (*AARD*), coefficients of determination (R^2), root mean square error (*RMSE*) and mean absolute error (*MAE*) which are defined as follows, respectively:

$$AARD\% = \frac{100}{n} \sum_{i=1}^{n} \frac{\left| N_{\exp_i} - N_{cal_i} \right|}{N_{\exp_i}} \tag{24}$$

$$R^2 = 1 - \frac{\sum_{i=1}^{n} \left[N_{\exp_i} - N_{cal_i} \right]^2}{\sum_{i=1}^{n} \left[N_{\exp_i} - N_m \right]^2} \tag{25}$$

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left(N_{\exp_i} - N_{cal_i} \right)^2} \tag{26}$$

$$MAE = \frac{\sum_{i=1}^{n} \left| N_{\exp_i} - N_{cal_i} \right|}{n} \tag{27}$$

where

$$N_m = \frac{\sum_{i=1}^{n} N_{\exp_i}}{n} \tag{28}$$

where N_{exp} and N_{cal} are the experimental and calculated value of the desirable quantity, respectively and n is the number of experimental data.

3. Experimental

The pervaporation experiments were conducted to separate ethanol (99.8%, Merck, Darmstadt, Germany) and water (deionized laboratory water) mixtures using a composite PDMS/PVDF/PP membrane with active layer thickness of 10 µm (Helmholtz–Zentrum Geesthacht Zentrumfür Material und Küstenforschung GmbH, Geesthacht, Germany). The pervaporation apparatus has been previously described [34,35]. The total flux (*J*) was calculated using the following equation:

$$J = \frac{W}{S\, t} \tag{29}$$

where *W* is weight of the collected permeate, *S* is area of the membrane (137.75 cm^2) and *t* is time duration of the experiments. The ethanol concentrations in the permeate was analyzed in triplicate using a Gas Chromatography (Younglin 6000M Series Gas Chromatography System, Anyang, Korea) by the procedure was described in detail elsewhere [14].

To determine the amount of ethanol/water mixture absorbed in the PDMS layer of the composite membrane, swelling measurements of the membranes were performed using a well-known gravimetric procedure [14].The sorption experiments were performed for the feed temperature of 30, 45 and 60°C and the feed ethanol concentration of 2,5, 25, 50 and 70%wt. The sorption results were reported as the ratio of the liquid weight sorbed per gram of dry membrane as follow:

$$w^s = \frac{w_s - w_d}{w_s} \tag{30}$$

where w^S is the weight fraction of the sorbed liquid in the swollen membrane, w_d and w_S denote the weight of dry and swollen membranes, respectively.

In this work, the effects of the feed ethanol concentration (2, 5, 25 and 50%wt.) and the feed temperature (30, 45 and 60°C) on the permeation flux and the ethanol concentration at the permeate side pressure of 1 mm Hg and the feed flow rate of 97.8 kg/h were determined. All experimental conditions were repeated three times and the average values are reported. Steady-state permeation was reached at the second hour of all experimental conditions. The time duration of each experiment was 8 h and a permeate sample was collected every one hour.

4. Results and discussion

4.1. 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. Fig. 3 depicts the effects of feed ethanol content on the amount of components taken by the PDMS membrane at temperature of 60°C. As shown in Fig. 3a, both experimental and modeling results indicate that an increase in the ethanol feed concentration contributes to intensive enhancement of sorbed ethanol in the hydrophobic membrane. Since the applied membrane is hydrophobic and non-polar, this membrane has greater tendency to take substances which have 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 Fig. 3b, 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 will. Hence, at low ethanol feed content, the water molecules have higher activity, consequently exhibit higher sorption. Moreover, the plasticization effect exerted by the presence of a small amount of ethanol also enhances the water molecules taken.

Fig. 4 indicates the effect of feed temperature on the sorption behavior of ethanol and water in the membrane for a 2%wt. ethanol feed solution. All sorption increases with the temperature. According to the free volume [36], an enhancement in feed temperature leads to increase the thermal motion of the polymer chains and thus more free volume is generated in the polymer matrix to facilitate the sorption of permeants in the membranes. Therefore, the sorption of both ethanol and water molecules enhances as the feed temperature goes to higher levels.

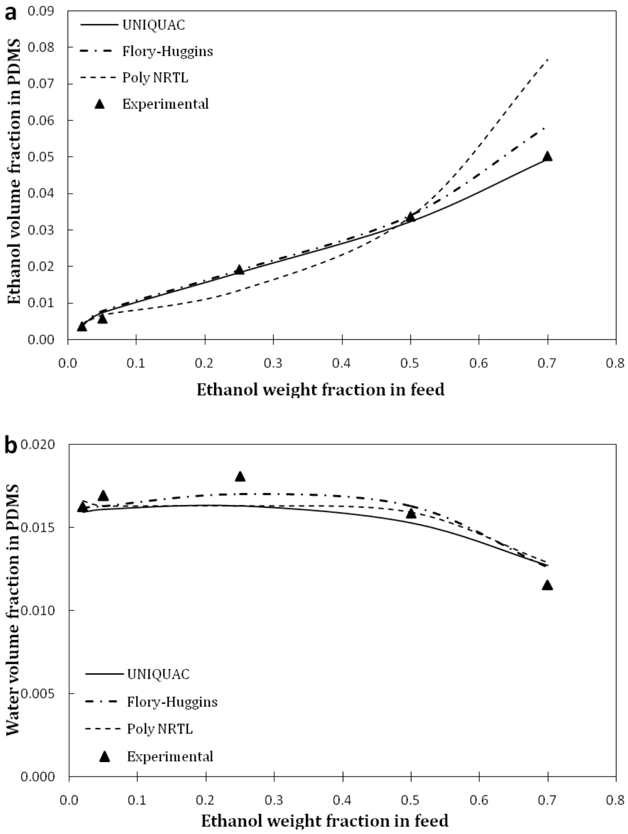

Fig. 3. The effect of feed ethanol content on the sorption of ethanol (a) and water (b) in the membrane at temperature of 60°C.

4.2. Pervaporation through the membrane

According to the solution-diffusion model, the transport and separation proprieties of the membrane were characterized by the sorption and diffusion in the membrane. Variation in the feed composition and temperature directly impresses the sorption phenomena at the feed/membrane interface as well as the diffusion of components through the membrane. Furthermore, the feed composition and temperature strongly affect the membrane swelling, concentration polarization and coupling phenomena which play important roles in the pervaporation process. Thus, the feed temperature and concentration are two important operating parameters for the pervaporation. In the following, the influences of these two variables on the separation performance of the pervaporation are investigated using the modeling and experimental data.

The influence of ethanol content in the feed solution on the pervaporation performance at a feed temperature of 60°C is shown in Fig. 5. The ethanol flux was increased by increasing the feed ethanol concentration from 2 to 50%wt., as shown in Fig. 5a. Based on the experimental and modeling results, the ethanol permeation flux through the PDMS membrane was linearly dependent on the ethanol feed content. Slater et al. [37], Li and Wang [38] and Shi et al. [39] have similarly reported the same trend for the ethanol flux through the PDMS membrane. Increasing ethanol partial flux with an enhancement in the feed ethanol content can be related to the driving force for the permeation and the transport properties of the membrane. As mentioned before, the chemical potential was chosen to describe the driving force of the pervaporation process. The chemical potential of a

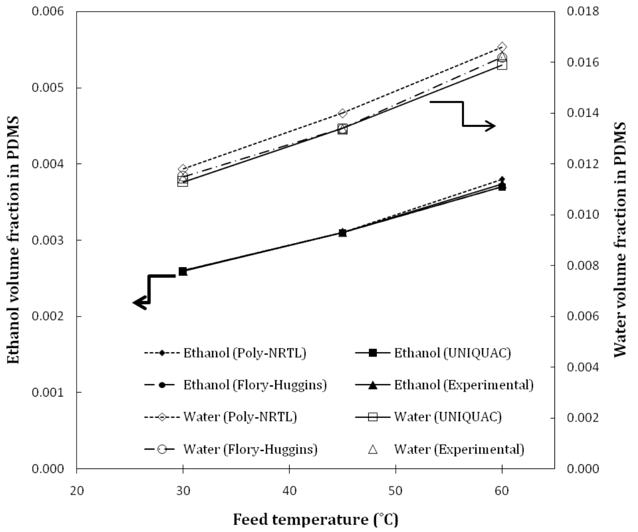

Fig. 4. The effect of feed temperature on the sorption of ethanol and water in the membrane for a 2 %wt. ethanol feed solution.

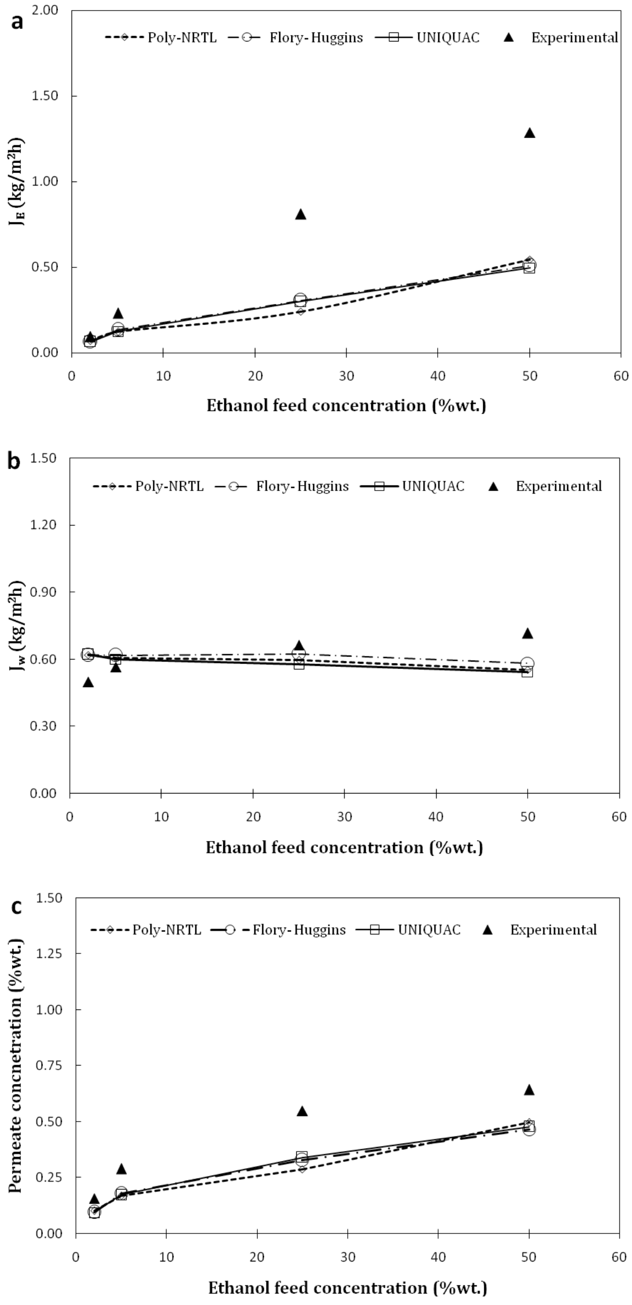

Fig. 5. The effect of feed concentration on the separation performance of pervaporation at temperature of 60°C: (a) ethanol flux, (b) water flux and (c) ethanol permeate concentration.

penetrant is directly affected by its concentration. Increasing the feed ethanol content leads to enhancement of the chemical potential gradient across the membrane, thereby increasing the permeation flux. Moreover, the penetrant concentration affects the mass transfer behavior due to the sorption and diffusion dependence on the penetrant concentration inside the membrane. As mentioned earlier, in the sorption step, a higher feed ethanol concentration will increase the sorption uptake of ethanol in the membrane (Fig. 3a). Consequently, the concentration of the penetrant inside the membrane will go to a higher level. Also, a high concentration of the penetrant inside the membrane leads to the membrane swelling. The membrane swelling will increase the free volume in the polymer matrix of the membrane, making it easier for ethanol to diffuse through the membrane, and thus higher permeation fluxes can be observed.

As can be seen in Fig. 5b, the water flux slightly increased with an enhancement in the feed ethanol concentration. The experimental results indicate that variations in the feed concentration from 2 to 50%wt. lead to enhancement in the water partial flux from 0.500 to 0.716 kg/m^{2}h. When the ethanol feed concentration increases or the water concentration decreases the lower sorption of water molecules into the membrane occurs as illustrated in Fig. 3b. On the other hand, higher ethanol sorption into the membrane due to higher ethanol concentration in the feed solution leads to the membrane swelling, thus the water molecules can easily pass through the swollen membrane. Therefore, an increase in the ethanol content of the feed solution results in decreasing water sorption and increasing water diffusion and consequently these two adverse phenomena cause slight increase in the water partial flux through the membrane.

The dependence of ethanol permeate concentration on the feed concentration is depicted in Fig. 5c. Both the modeling and experimental results indicate that the permeate concentration increases with an increment in the ethanol content of feed. When the ethanol feed concentration enhances, the ethanol partial flux significantly increases while the partial flux of water slightly enhances. Therefore, the greater amount of the ethanol permeation through the membrane in comparison to the water permeation leads to higher ethanol concentration in the permeate.

The influence of feed temperature on the pervaporation performance for separation of ethanol from a 50%wt. ethanol aqueous solution is shown in Fig. 6. The partial fluxes of ethanol and water increased when the feed temperature enhanced, as shown in Figs. 6a and 6b. The enhancement in the partial fluxes with an increment in the feed temperature may be attributed to changing in the driving force of the pervaporation process with temperature. As the vapor pressure of the permeating molecules varies with temperature, the feed temperature affects the driving force of the process. An increase in the vapor pressure of the pure component due to the enhancement in temperature, results in higher permeation flux through the membrane. In addition, a temperature variation in the feed solution affects the diffusivity and viscosity of components in the feed solution as well as the permeability of the membrane. Based on the free volume theory in the polymeric membrane, there are several free volumes between the polymer chains in the polymeric matrix which can be made from segmental motions of the polymer chain in the amorphous regions. The diffusing molecules penetrate through these free volumes in the polymeric membrane. The segmental motions into the polymer chain will be increased, as the feed temperature goes to a higher degree. As a result, the free volumes in the membrane increases, thus the diffusion rate of the individual permeating molecules increases, leading to a high permeation flux as the temperature increases. These results are in good agreement with results acquired by other researchers [37–40].

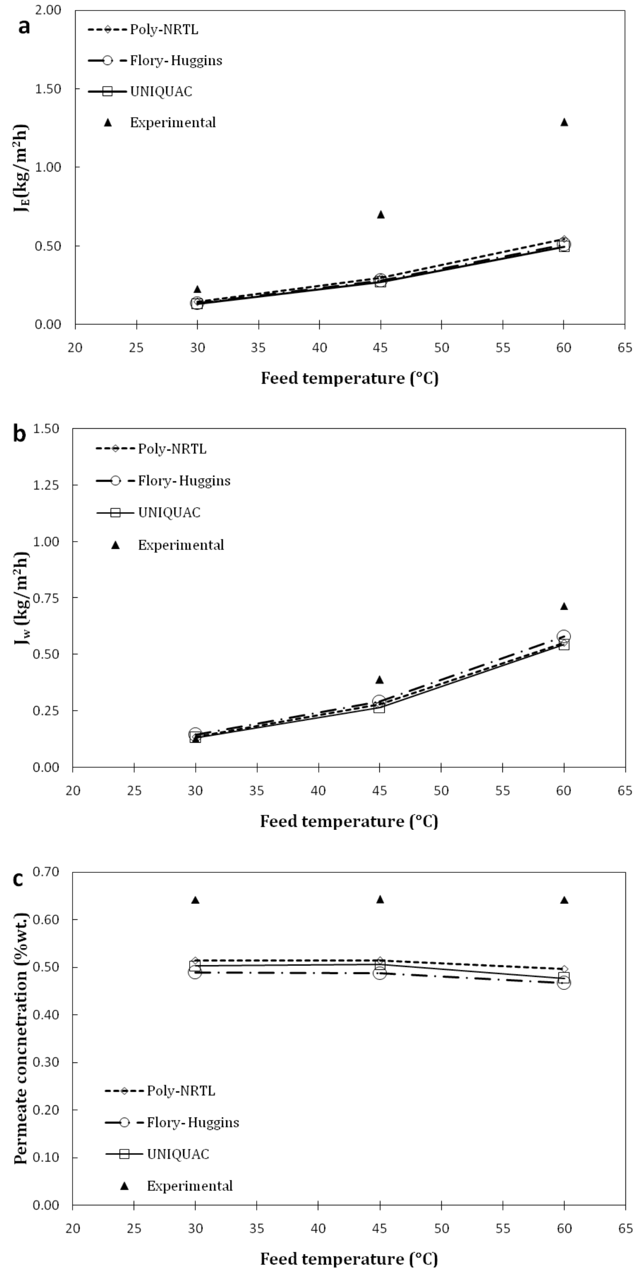

Fig. 6. The effect of feed temperature on the separation performance of pervaporation for a 50 %wt. ethanol feed solution: (a) ethanol flux, (b) water flux and (c) ethanol permeate concentration.

Fig. 6c shows that the ethanol permeate concentration does not change significantly at different temperatures for a 50%wt. ethanol aqueous solution. According to Figs. 5a and 5b, the water and ethanol fluxes increase at the same rate, when the feed temperature enhances. As the feed temperature varied from 30 to 60°C, the water and ethanol fluxes increase from 0.128 to 0.716 kg/m^{2}h and from 0.230 to 1.290 kg/m^{2}h, respectively. Therefore, the ethanol permeate concentration approximately remains constant by an increase in the feed temperature.

4.3. Model validation

In this section, the proposed model is validated by comparing with the experimental data. It can be seen from Fig. 3a that three applied thermodynamic models could successfully predict the amount of ethanol sorbed into the PDMS membrane. Among them, the sorption values obtained by the UNIQUAC equation were in completely agreement with the experimental data for all feed ethanol concentrations. Moreover, the results of Flory-Huggins theory had a great agreement in various ethanol concentrations except for 70%wt. ethanol feed concentration which is highly concentration feed. The poly-NRTL theory was able to estimate the amount of sorbed ethanol into the PDMS at dilute feed solutions, although the model had not enough accuracy for the concentrated feed solutions.

For modeling the water sorption from aqueous ethanol solutions into the membrane, The UNIQUAC equation was capable of determining the water volume fractions in the PDMS membrane when the ethanol feed mixtures are either highly diluted or highly concentrated, as can be seen from Fig. 3b. Further to the UNIQUAC model, the water sorption values predicted by the Flory-Huggins theory were in good agreement with the experimental observations for the whole feed concentration range. Also, the results of the poly-NRTL model had a good agreement with the experimental data when the feed is dilute. Moreover, it can be seen from Fig. 4 that all selected models were reasonably able to predict the temperature dependency of the sorption behavior in the hydrophobic membrane with appropriate accuracy in comparison to the experimental data. Similar results have been found in the literature for the sorption of various components in the polymeric membranes. For example, Jonquieres et al. [21] found that the UNIQUAC and related models were to be much more accurate than the Flory-Huggins theory for the vapors sorption of ether, ester and alcohol in polar elastomers. Yang and Lue [22] for the sorption behaviors of ethanol/water mixtures in the PDMS films observed that the UNIQUAC-HB model is advantageous over the classic UNIQUAC model and the Flory-Huggins equation because the UNIQUAC-HB model is able to predict the synergistic effect of ethanol on the solubility of water.

Besides, the compression between the pervaporation experimental data and the proposed mass transfer model based on three selected thermodynamic equations revealed that all three models could describe the effect of feed concentration on the ethanol partial flux and permeate concentration as indicated in Fig. 5a and 5c. The proposed thermodynamic models predicted the increase trend in the ethanol flux and permeate concentration and the high accuracy was observed when the feed ethanol concentration was low as concentration generally available for the pervaporation process. It was also found that the models were able to determine the effect of feed temperature on the partial fluxes of ethanol and water as well as on the ethanol concentration of the permeate (Fig. 6). Similar to the experimental data, the predicted water flux enhanced with increasing the feed temperature. The proposed models had also a reasonable agreement with experimental observations for the ethanol flux,especially for the feed temperature closed to the room temperature (Fig. 6a).

Finally, overall efficiency of the selected thermodynamic models for the sorption behavior of components into the pure PDMS membrane in term of the equilibrium volume fraction of the permeating compounds as well as for the pervaporation of ethanol/water mixtures with the composite PDMS membrane which is evaluated with the permeation flux and ethanol permeate concentration was checked by the *AARD* values and the results are presented in Fig. 7. As can be seen from this figure, the sorption step for all feed ethanol concentrations and feed temperatures indicated that the UNIQUAC equation is preferable model compared to the poly-NRTL and Flory-Huggins theories. Also, the values of R^2, *RMSE* and *MAE* for the predicted sorption of the ethanol/water solutions into the PDMS membrane are given in Table 3. The statistical results (Table 3) show that the three selected thermodynamic models can predict the sorption of the ethanol/water solutions into the PDMS, but the accuracy of the UNIQUAC model is higher than the Flory-Huggins and poly-NRTL models. Furthermore, there was no significant difference between the models abilities regarding the flux and permeate concentration.

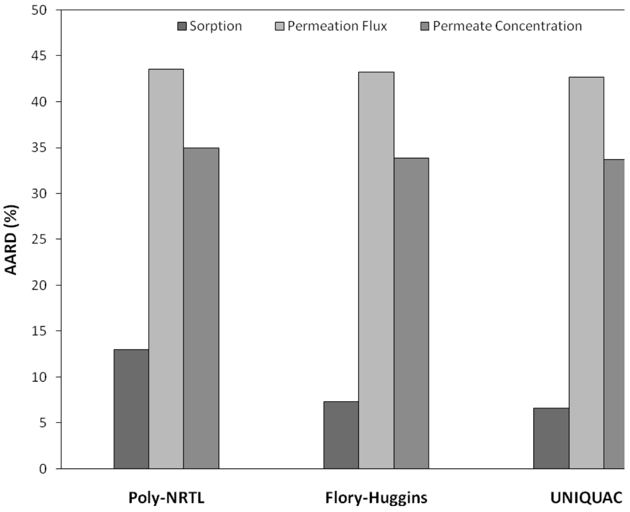

Fig. 7. Overall efficiency of three thermodynamic models regarding the average error.

5. Conclusions

A mass transfer model was developed for the hydrophobic pervaporation process based on the solution-diffusion theory using a thermodynamic model, generalized Fick's law and Duda's free volume theory. The UNIQUAC, Flory-Huggins and poly-NRTL thermodynamic models were employed to determine the activities and volume fraction of the permeating compounds in the membranes. The proposed model was validated using the experimental data from sorption and pervaporation of ethanol/water mixtures with the PDMS membranes. The model enables to describe the effects of major operating parameters such as the feed concentration and temperature on the partial fluxes and ethanol permeate concentration. The results showed that as the ethanol concentration in the feed solution increased, the partial fluxes and ethanol permeate concentration enhanced. The predicted and experimental permeation fluxes all increase with an increase in the feed temperature.

Moreover, three applied thermodynamic models could successfully predict the amount of ethanol sorbed by the pure PDMS membrane, and the sorption values obtained by the UNIQUAC equation were thoroughly agreement with the experimental data in all ethanol feed concentrations. The Flory-Huggins theory could predict the ethanol sorption in a good agreement with the experimental results for various ethanol concentrations except for 70% wt. ethanol feed concentration that is highly concentrated feed solution, while the poly-NRTL theory was able to estimate the amount of sorbed ethanol and water into the PDMS for dilute solutions and this model had not enough accuracy for the concentrated feed solutions. Also, the sorption behavior of water that modeled by the UNIQUAC and Flory-Huggins theories was in good agreement with the experimental data.

Besides, it was observed that there were no significant differences between the selected thermodynamic theories for the modeling of pervaporation process. Finally, it can be concluded that the UNIQUAC model is found to be much more accurate than the Flory-Huggins theory and the poly-NRTL model which is the modified form of the classic NRTL model for phase equilibria of the polymeric

Table 3
The statistical parameters to predict the sorption of the ethanol/water solutions into the membrane by various thermodynamic models

		R^2			RMSE			MAE		
		T = 30°C	T = 60°C	T = 45°C	T = 30°C	T = 60°C	T = 45°C	T = 30°C	T = 60°C	T = 45°C
UNIQUAC	Ethanol	0.996	0.00077	0.00059	0.00054	0.00100	0.00079	0.00073	0.997	0.997
	Water	0.933	0.00070	0.00035	0.00044	0.00093	0.00057	0.00079	0.923	0.939
	Total	0.986	0.00115	0.00092	0.00097	0.00156	0.00119	0.00132	0.990	0.992
Flory-Huggins	Ethanol	0.997	0.00051	0.00039	0.00038	0.00089	0.00076	0.00071	0.997	0.997
	Water	0.913	0.00044	0.00021	0.00033	0.00059	0.00035	0.00069	0.929	0.958
	Total	0.991	0.00070	0.00055	0.00069	0.00092	0.00082	0.00108	0.997	0.996
Poly-NRTL	Ethanol	0.977	0.00134	0.00097	0.00096	0.00261	0.00179	0.00183	0.978	0.985
	Water	0.865	0.00056	0.00039	0.00046	0.00086	0.00064	0.00084	0.875	0.878
	Total	0.944	0.00165	0.00136	0.00142	0.00339	0.00237	0.00263	0.954	0.969

systems. Among these thermodynamic models, the Flory-Huggins theory is mainly preferred due to its much greater simplicity.

Symbols

a_i — Activity of component i (–)
$AARD$ — Average absolute relative deviation (%)
D_i — Diffusion coefficient of component i into the membrane (m^2/s)
E_i — The critical energy of component i (cal/mol)
J_i — Mass flux of component i (kg/m^2s)
l_i — UNIQUAC parameter (–)
MAE — Mean absolute error (–)
n — Number of data (–)
N — Number of elements (–)
P — Pressure of the system (bar)
q_i — Molecular surface area for the pure component i (–)
R — Gas universal constant (J/mol K)
R^2 — Coefficients of determination (–)
r_i — Molecular Van der Waals volume for the pure component i
$RMSE$ — Root mean square error (–)
S — Area of the membrane (m^2)
T — Absolute temperature (K)
t — Time duration of experiment (h)
u_1 — Water volume fraction in the ethanol/water mixtures in the polymer (–)
u_2 — Ethanol volume fraction in the ethanol/water mixtures in the polymer (–)
V — Molar volume (m^3/mol)
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 — Weight fraction of the sorbed liquid in the swollen membrane (–)
x_i — Mole fraction of component i (–)
z — Penetration direction (m)
Z — Coordination number (–)

Greek

α_{ij} — Non-randomness factor (–)
Γ — Overlap factor (–)
θ — Surface fraction (–)
ξ_{ip} — Ratio of critical molar volume of jumping unit of component i (–)
ρ — Density (kg/m^3)
τ_{ij} — Binary interaction parameter of UNIQUAC and poly-NRTL model (–)
ϕ — Volume fraction (–)
χ_{ij} — Solvent/solvent interaction parameter (–)
χ_{ip} — Solvent/polymer interaction parameter (–)
δ — Membrane thickness (m)

Subscripts and superscripts

1 — Water
2 — Ethanol
3 — PDMS membrane
C — Combinatorial term
i — Component index
f — Feed
m — Membrane
p — PDMS membrane
P — Permeate
R — Residual term

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