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Pervaporation properties of PDMS membranes for removal of benzene from aqueous solution: Experimental and modeling

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Abstract

Polydimethylsiloxane (PDMS) pervaporation membranes were employed to remove benzene from aqueous solution. A predictive model was proposed based on solution-diffusion mechanism to predict mass transfer during pervaporation process. The solubility of components in the membrane was described by UNIFAC-FV model, and the diffusion coefficients in polymeric membrane were calculated by free volume theory. The effects of feed concentration and operating temperature on pervaporation properties were investigated to validate the model. It has shown that the proposed model can be applied to select membrane materials and predict the permeation flux and selectivity of components through the polymeric membrane.

Keywords: Pervaporation; PDMS; Solution-diffusion model; UNIFAC-FV; Free volume theory

1. Introduction

Pervaporation has become one of the most promising candidates for low-cost and environment-benign separation process, especially for separation of azeotropic or close-boiling liquid mixtures. Its application fields can be found in: (a) dehydration of organic/water mixtures, (b) removal or recovery of organic components from water and (c) separation of organic/organic mixtures.

There are two crucial issues for industrial application of pervaporation process. The first is developing membrane material and tailoring membrane structure to obtain high pervaporation properties. The second is modeling pervaporation transport to better understand of the above-mentioned structure–pervaporation relationship.

The molecule transport through the membrane has been studied quite extensively [1]. Many models were proposed to predict the mass transfer process, such as solution-diffusion model [2], thermodynamics of irreversible process [3], Maxwell–Stefan theory [4], pore flow model [5], pseudo phase change solution-diffusion model [6], resistance-in-series model [7] and molecular simulation [8]. Among them, solution-diffusion model is most widely used in describing pervaporation transport including preferential sorption, diffusion and evaporation steps. In recent years, considerable attention has been focused on the mass transfer behavior because of its vital role for optimizing pervaporation process.

For modeling pervaporation transport, the permeation flux, which depends on the solubility and diffusivity of components in the membrane, should be obtained first. Traditionally, the solubility was calculated according to the Flory–Huggins theory. However, the interaction parameter χ with strong temperature and concentration dependence had to be determined through experiments, which limited its predictive capability. Recently, group contribution methods had been successfully applied to predict activity coefficients in polymer solution. Fredenslund et al. [9] developed the UNIFAC model to calculate VLE for normal fluid systems. Oishi and Prausnitz [10] proposed the UNIFAC-FV model by adding a free volume term into the UNIFAC model, which could be used to both the polymer and polymer solutions. For the diffusivity, the predictive methods of component diffusion in polymer solution had been commonly studied [11]. And the free volume theory [12] was often used to describe the diffusion process of penetrants in polymer above the glass transition temperature.

In this study, a predictive model is established based on UNIFAC-FV model and free volume theory to predict the pervaporation properties of polymeric membrane simply using the

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Nomenclature

A_{d}	free volume parameters
A_{mn} A_{nm}	the group interaction parameters
a_i	activity of component i
a_i^{C}	activity of component i from combinatorial contribution
$a_i^{\mathrm{C+FV}}$	activity of component i from combinatorial contribution including free volume contribution
a_i^{FV}	activity of component i from free volume contribution
a_i^{R}	activity of component i from residual contribution
a_i^{l}	activity of component i in the feed
a_i^{m}	activity of component i in the feed side surf ace of the membrane
B_{d}	free volume parameters
c	concentration of feed (g benzene/g water)
D_{T}	thermodynamic diffusion coefficient of component i ($\mathrm{m^2\,s^{-1}}$)
D_i	diffusion coefficient of component i ($\mathrm{m^{-2}\,s^{-1}}$)
f	fractional free volume of component i
J_i	permeation flux of component i ($\mathrm{g\,m^2\,h^{-1}}$)
n	monomer number in a chain molecule
q_i	relative surface parameter of component i
R	gas constant ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
$r(1)$	volume parameter for the monomer
r_i	relative volume parameter of component i
T	temperature (K)
T_{g}	glass transition temperature (K)
V_i	molar volume of component i ($\mathrm{m^3\,mol^{-1}}$)
x_i	mole fraction of component i
Z	co-ordination number UNIFAC (commonly $Z=10$)
α	separation factor
β_i	proportional constant of component i
$\delta_{i\mathrm{d}}$	dispersion-forces component
$\delta_{i\mathrm{p}}$	polar component
$\delta_{i\mathrm{h}}$	hydrogen-bonding component
ρ_i	the density of component i
ϕ_{c}	crystallinity of polymer
ϕ_i	volume fraction term of component i in UNIFAC model
ϕ_i'	volume fraction term of component i in modified UNIFAC model
v_f	specific volume of component i
v_0	specific volume of component i at zero (K)
θ_i	surface fraction of component i
$v_k^{(i)}$	number of group k in molecular i
Γ_k	interaction activity of group k in the penetrant–polymer mixture
$\Gamma_k^{(i)}$	interaction activity of group k in pure component i

chemical structure and physical property parameters of polymer. In addition, the effects of feed concentration and operating temperature on permeation flux and selectivity through polydimethylsiloxane (PDMS) membrane were investigated to validate the model.

2. Theory

2.1. Modeling of solution

Based on the solution-diffusion model, it is assumed that swelling equilibrium is reached at the interface between the feed mixture and the polymeric membrane. The volume fraction of component i in the membrane can be obtained according to the chemical potential equilibrium.

The chemical potential at a given temperature and pressure can be expressed as the function of activity a_i.

$$\mu_i - \mu_i^0 = RT\ \ln a_i \tag{1}$$

There are thermodynamic phase equilibrium between the feed mixture and the polymeric membrane, which indicate that the chemical potential in both phases for component i is equal.

Based on Eq. (1), the equality of chemical potential can be expressed by activity equilibrium.

$$a_i^{\mathrm{l}} = a_i^{\mathrm{m}} \tag{2}$$

2.1.1. Calculation of the activity of components in the feed

UNIFAC group contribution method is introduced to calculate the activity of component i in the feed mixture [9], which is described as the sum of a combinatorial part (a_i^{C}) and a residual part (a_i^{R}).

$$\ln a_i = \ln a_i^{\mathrm{C}} + \ln a_i^{\mathrm{R}} = \ln \gamma_i^{\mathrm{C}} + \ln \gamma_i^{\mathrm{R}} + \ln x_i \tag{3}$$

The combinatorial part can be calculated by

$$\ln \gamma^{\mathrm{C}} = \ln \frac{\phi_i}{x_i} + \frac{zq_i}{2} \ln\left(\frac{\phi_i}{\theta_i}\right) + l_i - \frac{\phi_i}{x_i}\sum_j x_j l_j \tag{4}$$

$$l_i = \frac{Z}{2}(r_i - q_i) - (r_i - 1) \tag{5}$$

where Z is the coordination number and usually taken equally taken equal to 10.0 [13,14]. ϕ_i and θ_i are the volume fraction and the surface fraction of component i, respectively.

$$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \tag{6}$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \tag{7}$$

where the parameters r_i and q_i can be found in the reference or calculated through group contribution method.

The residual part of the activity is [15]

$$\ln \gamma_i^{\mathrm{R}} = \sum_k v_k^{(i)}[\ln \Gamma_k - \ln \Gamma_k^{(i)}] \tag{8}$$

where $v_k^{(i)}$ is the number of group k in component i, $\Gamma_k^{(i)}$ the interaction activity of group k in pure component i and Γ_k is the interaction activity of group k in the penetrant–polymer mixture. Γ_k can be expressed by

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_m \theta_m \psi_{mk} \right) - \sum_m \left(\frac{\theta_m \psi_{mk}}{\sum_n \theta_n \psi_{nm}} \right) \right] \quad (9)$$

where θ_m is the surface area parameter for group k, x_m the surface area fraction of group m, ψ_{mn} and ψ_{nm} are given by the group interaction parameter A_{mn} and A_{nm}.

The residual part is calculated by the method of solubility parameter described by Vicente and Gottifredi [18].

$$\ln a_i^{\mathrm{R}} = \sum_{j \neq i} V_i \phi_j^2 \frac{\lfloor (\delta_{i\mathrm{d}} - \delta_{j\mathrm{d}})^2 + (\delta_{i\mathrm{p}} - \delta_{j\mathrm{p}})^2 + (\delta_{i\mathrm{h}} - \delta_{j\mathrm{h}})^2 \rfloor}{RT} \quad (17)$$

According to the theory of solubility parameter, the residual part of the feed mixture containing polar components can be calculated by Eqs. (18) and (19).

$$\ln a_1^{\mathrm{R}} = V_1 \varphi_3^2 \frac{\lfloor (\delta_{1\mathrm{d}} - \delta_{3\mathrm{d}})^2 + (T_0/T)((\delta_{1\mathrm{p}} - \delta_{3\mathrm{p}})^2 + (\delta_{1\mathrm{h}} - \delta_{3\mathrm{h}})^2) \rfloor}{RT} + V_1 \varphi_2 \varphi_3 \frac{\lfloor (\delta_{2\mathrm{d}} - \delta_{3\mathrm{d}})^2 + (T_0/T)((\delta_{2\mathrm{p}} - \delta_{3\mathrm{p}})^2 + (\delta_{2\mathrm{h}} - \delta_{3\mathrm{h}})^2) \rfloor}{RT} \quad (18)$$

$$\ln a_2^{\mathrm{R}} = V_2 \varphi_3^2 \frac{\lfloor (\delta_{2\mathrm{d}} - \delta_{3\mathrm{d}})^2 + (T_0/T)((\delta_{2\mathrm{p}} - \delta_{3\mathrm{p}})^2 + (\delta_{2\mathrm{h}} - \delta_{3\mathrm{h}})^2) \rfloor}{RT} + V_2 \varphi_1 \varphi_3 \frac{\lfloor (\delta_{1\mathrm{d}} - \delta_{3\mathrm{d}})^2 + (T_0/T)((\delta_{1\mathrm{p}} - \delta_{3\mathrm{p}})^2 + (\delta_{1\mathrm{h}} - \delta_{3\mathrm{h}})^2) \rfloor}{RT} \quad (19)$$

$$\psi_{mn} = \exp\left(-\frac{A_{mn}}{T} \right) \quad (10)$$

$$\psi_{nn} = \exp\left(-\frac{A_{nm}}{T} \right) \quad (11)$$

A_{mn} and A_{nm} are obtained from phase equilibrium data for mixture containing various functional groups.

2.1.2. Activity of components in the membrane

According to the UNIFAC-FV model, the activity of components in the membrane can be affected by three contributions: combinatorial-entropy, residual-enthalpy and free volume.

$$\ln a_i = \ln a_i^{\mathrm{C}} + \ln a_i^{\mathrm{R}} + \ln a_i^{\mathrm{FV}} \quad (12)$$

The combinatorial part can be calculated by the modification form of Kikic et al. [16].

$$\ln a_i = \ln a_i^{\mathrm{C+FV}} + \ln a_i^{\mathrm{R}} \quad (13)$$

The part of the combination of combinatorial-entropy and free volume is calculated by

$$\ln a_i^{\mathrm{C+FV}} = \ln \phi_i' - \frac{\phi_i'}{x_i} + 1 - \frac{z q_i}{2} \left[\ln\left(\frac{\phi_i}{\theta_i} \right) + 1 - \frac{\phi_i}{\theta_i} \right] \quad (14)$$

The method of Zhong et al. [17] is used to calculate the volume fraction ϕ_i' and ϕ_i.

$$\phi_i' = \frac{x_i r_i}{x_1 r_1 + x_2 r_2 + x_{\mathrm{p}}[0.6583 n r(1)]} \quad (15)$$

$$\phi_i = \frac{x_i r_i}{x_1 r_1 + x_2 r_2 + x_{\mathrm{p}}[n r(1)]} \quad (16)$$

where x_1, x_2 and x_{p} are the mole fractions of the components and polymer. r_1, r_2 and $r(1)$ are the volume parameter for the solvents and monomer of the polymer.

Therefore, the volume fraction of components at the upstream side surface of the membrane could be obtained from the activity equilibrium with the feed.

2.2. Modeling of diffusion in polymer

Free volume theory is widely used in predicting diffusion coefficients of small molecule through polymers. Diffusivity D can be expressed by the following equation [19].

$$D_{\mathrm{T}} = RTA_{\mathrm{d}} \exp\left(\frac{-B_{\mathrm{d}}}{f(1 - \phi_{\mathrm{c}})} \right) \quad (20)$$

where A_{d} and B_{d} are the parameters related to the shape and size of the diffusing molecule. The fractional free volume f is a function of volume fraction of component $i(\varphi_i)$ and temperature (T), ϕ_{c} is the crystallinity of the polymer.

A generalized parameter B is defined by

$$B = \frac{-B_{\mathrm{d}}}{(1 - \phi_{\mathrm{c}})} \quad (21)$$

Therefore, the Eq. (20) can be expressed to

$$D_{\mathrm{T}} = RTA_{\mathrm{d}} \exp\left(\frac{B}{f} \right) \quad (22)$$

The fractional free volume of the binary system can be determined by the following equation [20].

$$f(\varphi_i, T) = f(0, T) + \beta_i(T) \varphi_i \quad (23)$$

where $f(0,T)$ is the fractional free volume of the pure polymer itself, which can be determined by [20]

$$f(0, T) = 0.025 + a(T - T_{\mathrm{g}}) \quad (24)$$

The parameter a can be set to $4.8 \times 10^{-5}\,\mathrm{K}^{-1}$ when $T < T_g$, and $4.8 \times 10^{-4}\,\mathrm{K}^{-1}$ when $T > T_g$. $\beta(T)$ is the proportional constant which can be determined from the fractional free volume of pure liquid.

When $\varphi_i = 1$, Eq. (22) becomes:

$$f(1, T) = f(0, T) + \beta_i(T) \tag{25}$$

The fractional free volume in liquid $f(1,T)$, can be calculated by the equation proposed by Doollitle [21].

$$f(1, T) = \frac{v_f - v_0}{v_f} \tag{26}$$

where v_f is the specific volume of the liquid at some temperature and v_0 is the specific volume of the liquid extrapolated to the temperature T at zero K without a phase change in the form of a density function.

The diffusion coefficient of component i in j at infinite dilution of i (D_i^0) can be calculated by Wike–Chang method [22].

$$D_i^0 = \frac{7.4 \times 10^{-8} (\phi_j M_j)^{1/2} T}{\eta_j V_j^{0.6}} \tag{27}$$

When $\varphi_i = 0$, Eq. (19) becomes

$$D_i^0 = RTA_\mathrm{d} \exp\left(\frac{B}{f(0, T)}\right) \tag{28}$$

The free volume parameters A_d and B_d can be obtained by the Eqs. (27) and (28).

Diffusion coefficient of component i (D_i) can be related to the thermodynamic diffusion coefficient D_T.

$$D_i = (D_\mathrm{T})_i (1 - \varphi_i) \varphi_i \frac{\partial \ln a_i}{\partial \varphi_i} \tag{29}$$

As mentioned above, the activity of component i in the membrane can be calculated by UNIFAC-FV model. Therefore, the derivative of solvent activity $\frac{\partial \ln a_i}{\partial \varphi_i}$ by differentiating Eq. (13) is

$$\frac{\partial \ln a_i}{\partial \varphi_i} = \frac{\partial \ln a_i^{\mathrm{C+FV}}}{\partial \varphi_i} + \frac{\partial \ln a_i^{\mathrm{R}}}{\partial \varphi_i} \tag{30}$$

2.3. Calculation of permeation flux and separation factor

The permeation flux of components can be calculated with the method described by Stern et al. [23].

$$J_i = \frac{\rho_i}{l} \int_{\phi_{\mathrm{ip}}}^{\phi_{\mathrm{if}}} \frac{D_i}{1 - \phi_i} \, \mathrm{d}\phi_i \tag{31}$$

where J_i is the permeation flux of component i, l the membrane thickness, ϕ_{if} and ϕ_{ip} the volume fraction of component i at the upstream side and downstream side membrane interface, D_i is the diffusion coefficient of component i, and ρ_i is the density of component i.

The separation factor α can be calculated by

$$\alpha = \frac{J_1/J_2}{c} \tag{32}$$

where J_1 and J_2 are the partial pervaporation permeation flux of benzene and water, g/(m^2 h) and c is the concentration of feed, g (benzene)/g (water).

3. Experimental

3.1. Materials and membrane preparation

The PDMS prepolymer (the average molecular weight is 39700) was purchased from Beijing Chemical Co. Ltd. Methyltriethoxysilane prepolymer, dibutyltin diacetate, heptane and benzene were of analytical grade, and they were purchased from Tianjin Kewei Chemical Co. and used without further purification.

The PDMS membrane is prepared by phase inversion approach, dissolving the PDMS prepolymer, methyltriethoxysilane prepolymer (curing agent) and dibutyltin diacetate (catalyst) in *n*-heptane (solvent) in a certain proportion. Then the solution is cast on an organic glass plate and the solvent is evaporated at room temperature for 48 h. Finally, the membrane is peeled off from the organic glass plate. The thickness of the resultant membranes is about 140–200 μm.

3.2. Pervaporation experimental

The pervaporation apparatus is shown in Fig. 1, where the membrane cell is purchased from CM-Celfa AG Company, Switzerland and the effective membrane area is 28.0 cm^2. The downstream pressure is kept about 0.2 kPa. The permeate is collected by the cold trap, and then is dissolved in a specific amount of diethyl amino. The compositions of permeate are determined by gas chromatography (HP 6890) equipped with a flame ionization detector (FID).

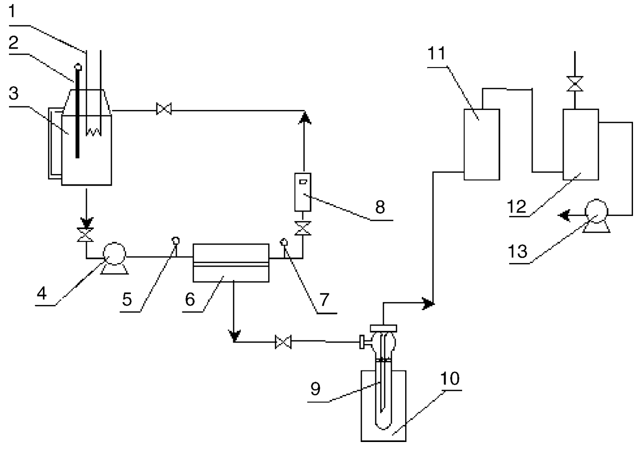

Fig. 1. The schematic diagram of the PV experimental equipment: (1) electric heater, (2) thermopair, (3) feed tank, (4) computation pump, (5 and 7) sample and temperature measuring point, (6) membrane cell, (8) rotor flow meter, (9) permeate collector, (10) cold trap, (11) drier, (12) buffer vessel, (13) vacuum pump.

3.3. *Definition of permeation flux and separation factor*

The permeation flux is given by

$$J_i = \frac{m_i}{At} \tag{33}$$

where J_i is the permeation flux of component i, g/(m^2 h); m_i the weight of component i in permeate, g; A the effective membrane area, m^2 and t is the permeation time, h.

The separation factor α is defined as follows:

$$\alpha = \frac{y_1/y_2}{x_1/x_2} \tag{34}$$

where x_1 and x_2 are the concentration of benzene and water in feed and y_1 and y_2 are the concentration of benzene and water in the permeate.

4. Results and discussion

4.1. *Effect of feed concentration on permeation flux and selectivity*

As shown in Fig. 2, the permeation flux of the benzene is much higher than the water, which shows that the PDMS membrane is preferentially permselectivity to benzene. And the permeate permeation flux increases obviously with benzene concentration increasing in feed, as a consequence of the polymer matrix swelling. On the other hand, this effect also causes more water easily through the membrane, which leads to separation factor decrease.

The permeation flux of total, benzene and water, and separation factor predicted by the proposed model are in good agreement with the experimental data at low feed concentration. But with the increase of the benzene concentration, the errors also increase. The experimental and predicted permeation fluxes of benzene and water are shown in Figs. 3 and 4. The permeation fluxes of benzene and water predicted are also higher than the experimental data. These errors may come from the supposed swelling equilibrium, which maybe not reached in the experiment. Therefore, the model overestimated the volume fraction of the components on the surface of the membrane. At low concentration of benzene, the swelling equilibrium is easy to reach; therefore, the predicted data and experimental data can be in good agreement. And at higher concentration the degree of non-equilibrium becomes more pronounced, which leads to a bigger calculation deviation. In addition, the concentration polarization in the pervaporation membrane process, which may also bring additional deviation, is not taken into account in this proposed model (Fig. 5).

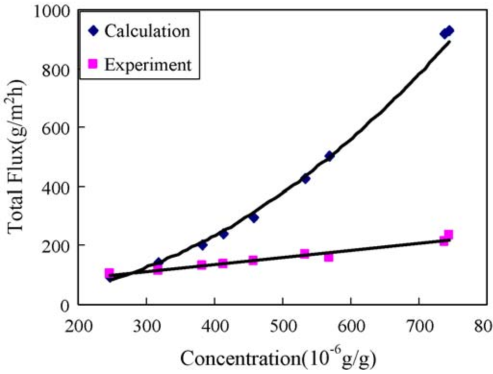

Fig. 2. Effect of benzene concentration in feed on experimental and predicted total flux.

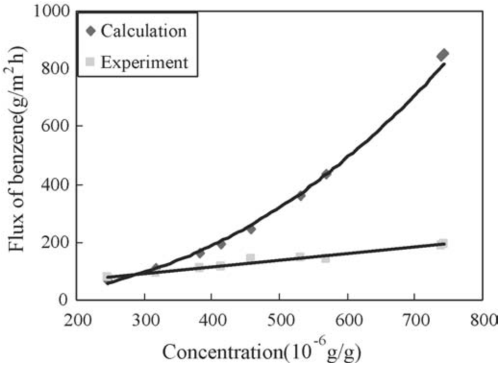

Fig. 3. Effect of benzene concentration in feed on experimental and predicted flux of benzene.

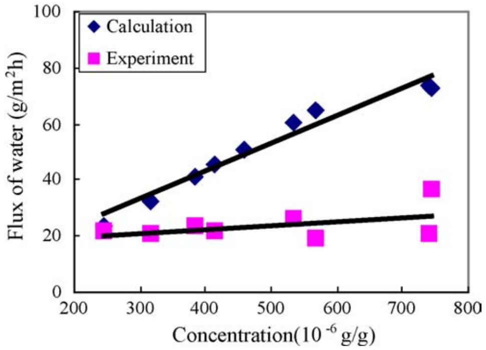

Fig. 4. Effect of benzene concentration in feed on experimental and predicted flux of water.

4.2. *Effect of temperature on permeation flux and selectivity*

The effects of operating temperature on permeation flux of total, benzene and water when benzene concentration

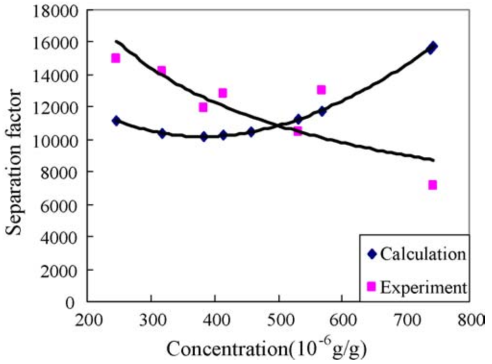

Fig. 5. Effect of benzene concentration in feed on experimental and predicted separation factor.

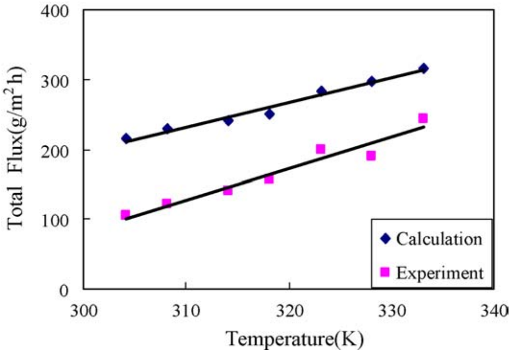

Fig. 6. Effect of temperature on experimental and predicted total flux.

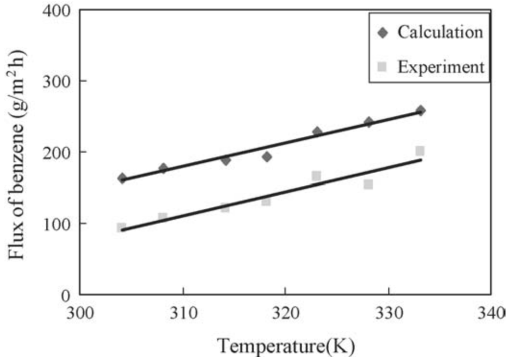

Fig. 7. Effect of temperature on experimental and predicted flux of benzene.

in feed is 440×10^{-6} g (benzene)/g (water) are shown in Figs. 6–8, respectively. The permeation flux of total, benzene and water all increase with operating temperature increasing. The predicted permeation fluxes are all higher than the experimental values, but they have the same changing trend. The deviation may also come from the supposed swelling equilibrium, which cannot actually realize in pervaporation experiment.

The separation factor predicted by the proposed model fits well with the experimental data at higher operating temperature. With operating temperature decreasing, the errors between predicted and experimental data increase. Deviation may be caused by water clustering, which diffuses not as single molecule but in its dimeric or trimetric form [24]. Clustering may not decrease the solubility of water in the membrane. But as its cross-section is larger than a single molecule, it will cause a noticeable reduction in the diffusivity of water in the membrane [25]. At lower operating temperature, the effect of water cluster is more obvious, and the deviation is thus bigger. With operating temperature increasing, the energy of water molecule increases and the effect of the water clustering decreases, which lead to the predicted separation factor by the proposed model-fitting better with the experimental results (Fig. 9).

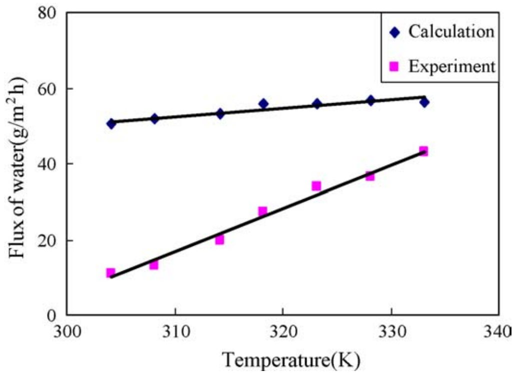

Fig. 8. Effect of temperature on experimental and predicted flux of water.

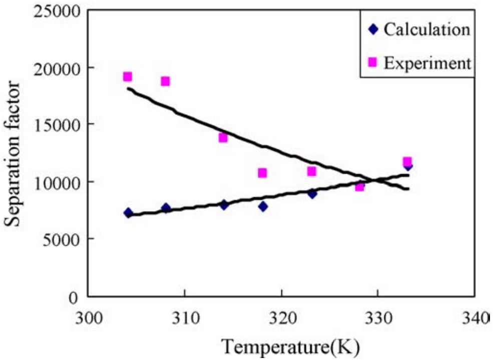

Fig. 9. Effect of temperature on experimental and predicted separation factor.

5. Conclusion

A model to predict the permeation flux and selectivity in the pervaporation process for removal of benzene from aqueous solution through PDMS membrane has been developed based on the solution-diffusion model. In the proposed model, UNIFAC-FV model and free volume theory are employed to describe the solubility and diffusivity of components in the membrane. The effects of feed concentration and operating temperature on the predicted permeation flux and separation factor by this proposed model are investigated. The predicted permeation fluxes and separation factor are in good agreement with experimental data at lower benzene concentration in feed, but at higher benzene concentration, the model overestimated permeation flux and separation factor. The predicted and experimental permeation fluxes all increase with operating temperature increasing. The predicted separation factor fits well with the experimental data at higher temperature, but at lower temperature, the model usually underestimated separation factor. The agreement between the predicted data and the experiment data is acceptable at higher temperature and the lower feed concentration. The model would be helpful to select the membrane materials due to its fully predictive characteristics.

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