

A Modified Solution–Diffusion Model and Its Application in the Pervaporation Separation of Alkane/Thiophenes Mixtures with PDMS Membrane

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ABSTRACT: A better understanding of the mass transfer in pervaporation membranes under different conditions is essential for both the design of improved membranes in various applications, and for the process design. In this article, a modified solution-diffusion model is proposed to account for the mass transport of penetrants in the polymer membrane. In the model, the group contribution method (the UNIFAC-ZM model) is first introduced to calculate the activity of penetrants in the polymer membrane, and a modified Fujita diffusion coefficient equation is developed to describe the diffusion behavior of the penetrants. The aim of this work is to establish a predictive solution-diffusion model. By refitting the group interaction

parameters based on pervaporation data of penetrants-membrane systems, the model can be applied to predict the flux and separation factor of various polymer membrane systems. As an exemplary application of the model, the permeation fluxes and separation factors of alkane/thiophene and alkane/2-methyl-thiophene mixtures in polydimethylsiloxane (PDMS) membrane system have been predicted and showed to be in good agreement with experimental values. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3140–3148, 2008

Key words: pervaporation; solution-diffusion model; group contribution method

INTRODUCTION

Pervaporation separation of liquid mixtures through polymeric membranes has been studied extensively and is considered as a prospective industrial separation process for a wide variety of liquid mixtures such as azeotropic, close boiling, heat sensitive, and ultra composition-asymmetric mixtures. A better understanding of the mass transfer in pervaporation membranes under different conditions is essential for both the design of improved membranes in various applications and for the process design.

A variety of models^{1–7} were used to describe the mass transport in pervaporation membrane. Among

these models, the following two are typical: the first is the solution-diffusion model, in which permeants dissolve in the membrane and then diffuse through the membrane down a concentration gradient. A separation is achieved between different permeants because of differences in the amount of permeant that dissolves in the membrane and the rate at which the permeant diffuses through the membrane. The second is the pore flow model, the distinguishing feature of which is that it assumes a liquid–vapor phase boundary inside the membrane, and pervaporation is considered to be a combination of liquid transport and vapor transport in series.

The solution-diffusion model, which has become the most popular model accepted by the majority of membrane researchers, was originally developed by Graham⁸ to describe the permeation of gases through dense membrane rubber septa. Binning et al.³ introduced the model to pervaporation. After that, many researches which were mainly focused on the diffusion of the penetrants were done to improve the model. Fels and Huang⁹ employed the free-volume theory of Fujita¹⁰ which was widely accepted for determining diffusion coefficients to calculate the separation factors and the permeabilities. Brun et al.¹¹ proposed a “six coefficients exponential model” for describing the binary transport in pervaporation membranes with moderate degrees of

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swelling. Shao and coworkers¹² simplified Brun's model by ignoring the plasticization effect of the less-permeable penetrants in the case of pervaporation dehydration of ethylene glycol. Schaetzel et al.¹³ assume that the diffusion coefficient is the product of a limit diffusivity and an analytic function depending only on the total volume fraction of all the penetrants in the membrane. Wijmans¹⁴ considered that the permeant molar volume in the membrane phase and the liquid phase are not equal and proposed the concept of the molar volume correction factor. Peng et al.¹⁵ developed a modified solution-diffusion model based on UNIFAC-FV model and free-volume theory. These researches have made contributions to the development of the solution-diffusion model. However, these models are not so predictive and confined to a limited systems to be analyzed.

In this article, a modified solution-diffusion model, in which the solution of penetrants in the membrane is mainly focused, is proposed to account for the mass transport of penetrants in the polymer membrane. In the model, the group contribution method (the UNIFAC-ZM model) is first introduced to calculate the activity of penetrants in the polymer membrane, and a modified Fujita temperature-dependence diffusion coefficient equation is proposed to describe the diffusion behavior of the penetrants. The aim of this work is to establish a predictive solution-diffusion model. By refitting the group interaction parameters based on pervaporation data of penetrants-membrane systems, the model can be applied to predict the flux and separation factor of various polymer membrane systems. The model is applied to the prediction of the permeation fluxes and separation factors of alkane/thiophene and alkane/2-methyl-thiophene in polydimethylsiloxane (PDMS) membrane system, which was employed to simulate the desulfurization process of gasoline.

TRANSPORT MODEL

For one-dimensional steady-state mass transfer, the flux of a component i through the membrane is proportional to its chemical potential gradient.¹⁶

$$J_i = -\frac{D_{iM}^* c_i}{RT} \frac{\partial \mu_i}{\partial \delta} \quad i = 1, 2, \dots, n \quad (1)$$

where D_{iM}^* is the thermodynamic diffusion coefficient. μ_i is the chemical potential inside the membrane which can be described as

$$\mu_i = \mu_0 + RT \ln \alpha_i + V_i p \quad (2)$$

Substituting eq. (2) into eq. (1) gives

$$J_i = -\frac{D_{iM}^* c_i}{RT} \left(RT \frac{\partial \ln \alpha_i}{\partial \delta} + V_i \frac{dP}{d\delta} \right) \quad (3)$$

The pressure drop across the membrane is usually neglected as the solution-diffusion model assumes that the dense part of the membrane is entirely at the feed pressure. Thus, the following expressions can be obtained

$$J_i = -D_{iM}^* c_i \frac{\partial \ln \alpha_i}{\partial \delta} \quad (4)$$

Equation (4) can be represented as

$$\ln J_i = \ln D_{iM}^* + \ln \left(-c_i \frac{\partial \ln \alpha_i}{\partial \delta} \right) \quad (5)$$

In eq. (5), the flux of component i through the membrane is divided into a diffusion and solution part. The diffusion part can be calculated by the diffusion coefficient equation, and the solution part can be described by the activity model. The calculation of these two parts is represented later.

Calculation of diffusion coefficient

The thermodynamic diffusion coefficient based on the Fujita free-volume model¹⁰ can be described as

$$D_{iM}^* = A_{di} RT \exp \left(-\frac{B_i}{f(\phi_i, T)} \right) \quad (6)$$

where, $f(\phi_i, T)$ is a function representing the fractional free volume of the system which can be represented as

$$f(\phi_i, T) = f(0, T) + \beta(T) \phi_i \quad (7)$$

where $f(0, T)$ is the free-volume fraction of the polymer itself, and $\beta(T)$ is a temperature dependent coefficient.

In the Fujita model, three parameters (A_{di} , B_i , $\beta(T)$) are required to calculate the diffusion coefficient. In this work, based on data fitting, it is found that two parameters (A_{iM} , B_{iM}) in the following diffusion coefficient equation also can obtain good results. Therefore, the following temperature dependent diffusion coefficient equation is developed.

$$D_{iM}^* = A_{iM} RT \exp \left(-\frac{B_{iM}}{(T/273)^{1.5}} \right) \quad (8)$$

where A_{iM} and B_{iM} are model parameters characteristic of the interaction between penetrant i and the membrane M .

Calculation of activity

In this work, the group contribution method (the UNIFAC-ZM model¹⁷) is first introduced to calculate the activity of penetrants in the polymer membrane.

The Unifac-ZM model consists of a combinatorial and a residual part:

$$\ln a_i = \ln \gamma_i^c + \ln \gamma_i^{\text{res}} + \ln x_i \quad (9)$$

where the combinatorial part is given by:

$$\ln \alpha_i^c = \ln x_i \gamma_i^c = \ln \phi_i' + 1 - \frac{\phi_i'}{x_i} - \frac{Zq_i}{2} \left(\ln \frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i} \right) \quad (10)$$

where

$$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad (11)$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad (12)$$

$$\phi_i' + \frac{r_i x_i}{\sum_j \varepsilon_j r_j x_j} \quad (13)$$

In eq. (13), ε_j is equal to 1 and 0.6583 for penetrants and polymer membrane, respectively.

The residual part of the Unifac-ZM model is described as follows:

$$\ln \gamma_i^{\text{res}} = \sum_k v_k^{(i)} \left(\ln \Gamma_k - \ln \Gamma_k^{(i)} \right) \quad (14)$$

where $v_k^{(i)}$ is the number of group k in molecular i , Γ_k is the activity coefficient of group k at the mixture composition, and $\Gamma_k^{(i)}$ is the activity coefficient of group k at a group composition corresponding to pure component i .

The activity coefficient groups Γ_k are given by

$$\ln \Gamma_k = Q_k \left(1 - \ln \sum_m \Theta_m \Psi_{mk} - \sum_m \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}} \right) \quad (15)$$

where m and k are the number of groups in the solution, Θ_m is the group surface area fraction of group m in the given system, and Ψ_{mk} is the group interaction parameter for the interaction of group m with group k .

The group surface area fraction Θ_m for group m is given by

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad (16)$$

$$X_m = \frac{\sum_i x_i v_{mi}}{\sum_i x_i \sum_m v_{mi}} \quad (17)$$

where v_{mi} is the number of groups of type m in component i , m is the number of groups in the mixture, and x_i is the mole fraction of component i in the polymer solution.

The group interaction parameter Ψ_{mk} is given by as follows:

$$\Psi_{mk} = \exp\left(-\frac{a_{mk}}{T}\right) \quad (18)$$

where a_{mk} is the group interaction parameter for the interaction of group m with group k .

To calculate the flux of the penetrants, the derivative of the solvent activity should be obtained by differentiating eq. (9).

$$\frac{\partial \ln a_i}{\partial w_i} = \frac{\partial \ln \alpha_i^c}{\partial w_i} + \frac{\partial \ln \gamma_i^{\text{res}}}{\partial w_i} \quad (19)$$

The combinatorial part can be described by the derivative of eq. (10).

$$\begin{aligned} \frac{\partial \ln \alpha_i^c}{\partial w_i} &= \left(\frac{1}{\phi_i'} - \frac{1}{x_i} \right) \frac{\partial \phi_i'}{\partial w_i} + \frac{\phi_i'}{x_i^2} \frac{\partial x_i}{\partial w_i} \\ &\quad - \frac{Zq_i}{2} \left[\left(\frac{\theta_i}{\phi_i} - 1 \right) \left(\frac{\partial \phi_i}{\theta_i \partial w_i} - \frac{\partial \theta_i}{\partial w_i} \frac{\phi_i}{\theta_i^2} \right) \right] \end{aligned} \quad (20)$$

where

$$\frac{\partial \phi_i}{\partial w_i} = \frac{r_i (\partial x_i / \partial w_i)}{\sum_j r_j x_j} - \frac{r_i x_i \sum_j r_j (\partial x_j / \partial w_i)}{\left(\sum_j r_j x_j \right)^2} \quad (21)$$

$$\frac{\partial \theta_i}{\partial w_i} = \frac{q_i (\partial x_i / \partial w_i)}{\sum_j q_j x_j} - \frac{q_i x_i \sum_j q_j (\partial x_j / \partial w_i)}{\left(\sum_j q_j x_j \right)^2} \quad (22)$$

$$\frac{\partial \phi_i'}{\partial w_i} = \frac{r_i (\partial x_i / \partial w_i)}{\sum_j r_j x_j} - \frac{r_i x_i \sum_j r_j (\partial x_j / \partial w_i)}{\left(\sum_j r_j x_j \right)^2} \quad (23)$$

The derivative of the residual part can be obtained from eq. (14) as

$$\begin{aligned} \frac{\partial \ln \gamma_i^{\text{res}}}{\partial w_i} &= \sum_k v_k^{(i)} \left(\frac{\partial \ln \Gamma_k}{\partial w_i} - \frac{\partial \ln \Gamma_k^{(i)}}{\partial w_i} \right) \\ &= - \sum_k v_k^{(i)} Q_k \left[\frac{\left(\sum_m \Psi_{mk} \frac{\partial \Theta_m}{\partial w_i} \right)}{\sum_m \Theta_m \Psi_{mk}} \right. \\ &\quad \left. + \sum_m \frac{\Psi_{km} \left(\sum_n \Theta_n \Psi_{nm} \right) \frac{\partial \Theta_m}{\partial w_i} - \Theta_m \Psi_{km} \left(\sum_n \Psi_{nm} \frac{\partial \Theta_n}{\partial w_i} \right)}{\left(\sum_n \Theta_n \Psi_{nm} \right)^2} \right] \end{aligned} \quad (24)$$

where

$$\frac{\partial \Theta_m}{\partial w_i} = \frac{\Theta_m}{X_m} \frac{\partial X_m}{\partial w_i} - \frac{\Theta_m^2}{Q_m X_m} \left(\sum_n Q_n \frac{\partial X_n}{\partial w_i} \right) \quad (25)$$

in which

$$\frac{\partial X_m}{\partial w_i} = \frac{\sum_j v_{mj} \frac{\partial x_j}{\partial w_i}}{\sum_j x_j \sum_m v_{mj}} - \frac{\sum_i x_j v_{mj} \left(\sum_j \frac{\partial x_j}{\partial w_i} \sum_m v_{mj} \right)}{\left(\sum_j x_j \sum_m v_{mj} \right)^2} \quad (26)$$

In eqs. (21), (22), (23), and (26)

$$\frac{\partial x_i}{\partial w_i} = \frac{\frac{1}{M_i}}{\sum_i w_i / M_i} - \frac{\frac{w_i}{M_i} \left(\sum_j \frac{\partial w_j}{\partial w_i} / M_j \right)}{\left(\sum_i w_i / M_i \right)^2} \quad (27)$$

$$\frac{\partial x_j}{\partial w_i} = - \frac{w_j}{M_j} \frac{\left(\sum_j \frac{\partial w_j}{\partial w_i} / M_j \right)}{\left(\sum_i w_i / M_i \right)^2} \quad (28)$$

APPLICATION OF THE MODEL IN PERVAPORATION

The weight fraction of penetrant *i* in the membrane at the feed side and the permeate side of the pervaporation membrane are calculated as follows:

The concentration of the penetrants at the boundary of the membrane can be calculated from thermodynamic principles. At the membrane interface, the thermodynamic potentials of the membrane and its adjacent phase are assumed to be equal.

$$\mu_{f,i} = \mu'_{f,i} \quad (29)$$

$$\mu_{p,i} = \mu'_{p,i} \quad (30)$$

where $\mu'_{f,i}$ and $\mu'_{p,i}$ are the chemical potentials of penetrant *i* in the liquid feed and the permeate gas, respectively. $\mu_{f,i}$ and $\mu_{p,i}$ are the chemical potentials of penetrant *i* in the membrane at the feed side and the permeate side, respectively.

In the feed side, the chemical potentials can be described as follows:

$$\mu_{f,i} = \mu_0 + RT \ln a_{f,i} \quad (31)$$

$$\mu'_{f,i} = \mu_0 + RT \ln a'_{f,i} \quad (32)$$

Combining eqs. (29), (31), and (32) lead to

$$a_{f,i} = a'_{f,i} \quad (33)$$

where $a'_{f,i}$ is the activity coefficient of penetrant *i* in the liquid feed and can be calculated using the UNI-FAC model, whereas $a_{f,i}$ can be obtained from the UNIFAC-ZM model mentioned earlier. The weight fraction of penetrant *i* in the membrane at the feed side can be obtained based on eq. (33) and the UNI-FAC-ZM model.

In the permeate side, the chemical potentials can be described as follows:

$$\mu_{p,i} = \mu_0 + RT \ln \hat{f}_{p,i} \quad (34)$$

$$\mu'_{p,i} = \mu_0 + RT \ln \hat{f}'_{p,i} \quad (35)$$

where $\hat{f}_{p,i}$, $\hat{f}'_{p,i}$ are the fugacity of penetrant *i* in the membrane at the permeate side and in the permeate gas, respectively. Combining eqs. (30), (34), and (35) lead to

$$\hat{f}_{p,i} = \hat{f}'_{p,i} \quad (36)$$

where $\hat{f}'_{p,i} = \hat{\phi}_i y_i P$, $\hat{\phi}_i$ is the fugacity coefficient, and y_i is the mole fraction of *i* in the permeate gas. *P* is the system pressure. $\hat{\phi}_i$ is approximate to 1 at low pressure. Thus,

$$\hat{f}'_{p,i} = y_i P \quad (37)$$

In the membrane, at the permeate side and at low pressure

$$\hat{f}_{p,i} = P_i^{\text{sat}} x_i \gamma_i \quad (38)$$

where P_i^{sat} is the saturated vapor pressure of penetrant *i* and is calculated with the Antoine equation as follows:

$$\ln P_i^{\text{sat}}(\text{mmHg}) = A - \frac{B}{C + T/K} \quad (39)$$

The weight fraction of penetrant *i* in the membrane at the permeate side can be obtained by combining eqs. (36), (37), and (38).

EXPERIMENTAL

Membrane preparation

PDMS (viscosity 10 Pa, molecular weight 60,000), crosslinking agent ethyl orthosilicate, and catalyst dibutyltin dilaurate are dissolved in *n*-heptane at ambient temperature. After being degassed under vacuum, the solution is cast onto the PAN membrane. The membrane is first vulcanized under room temperature to evaporate the solvent and then introduced into a vacuum oven to complete crosslinking.

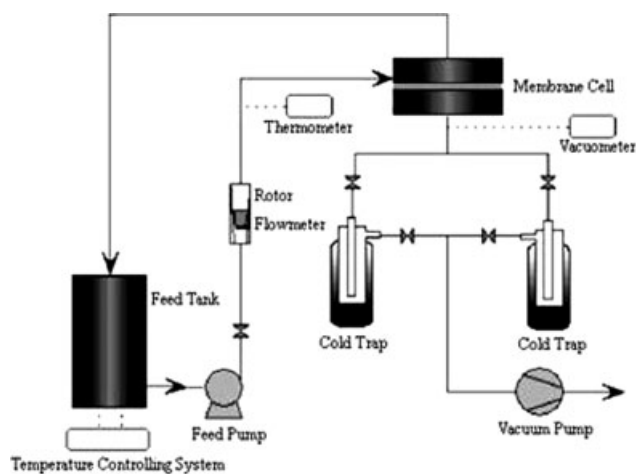


Figure 1 Scheme of the pervaporation apparatus.

Controlling the solution concentration or the coating amount could produce membranes with variable top layer thickness. The thickness of the top skin layer could be determined by means of SEM photographs. All experiments in this study are performed with the same membrane. The thickness of the membrane is about 11 μm .

Pervaporation experiments

A schematic layout of the experimental set-up used in this study is depicted in Figure 1. In the apparatus, a membrane supported by a porous sintered stainless steel in the permeate side is mounted in the pervaporation cell. The effective area of the membrane is $2.83 \times 10^{-3} \text{ m}^2$. The feed is heated and circulated from the feed tank (volume of $2.5 \times 10^{-3} \text{ m}^3$) through

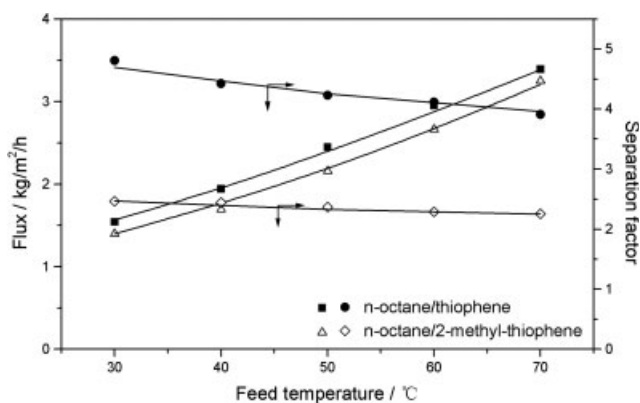


Figure 2 Temperature dependence of flux and selectivity for *n*-octane/thiophene and *n*-octane/2-methyl-thiophene mixture system. Thiophene and 2-methyl-thiophene content in feed: 0.364 wt % and 0.463 wt %, respectively. The curves are predicted with the solution-diffusion model. The symbols are the experimental data.²²

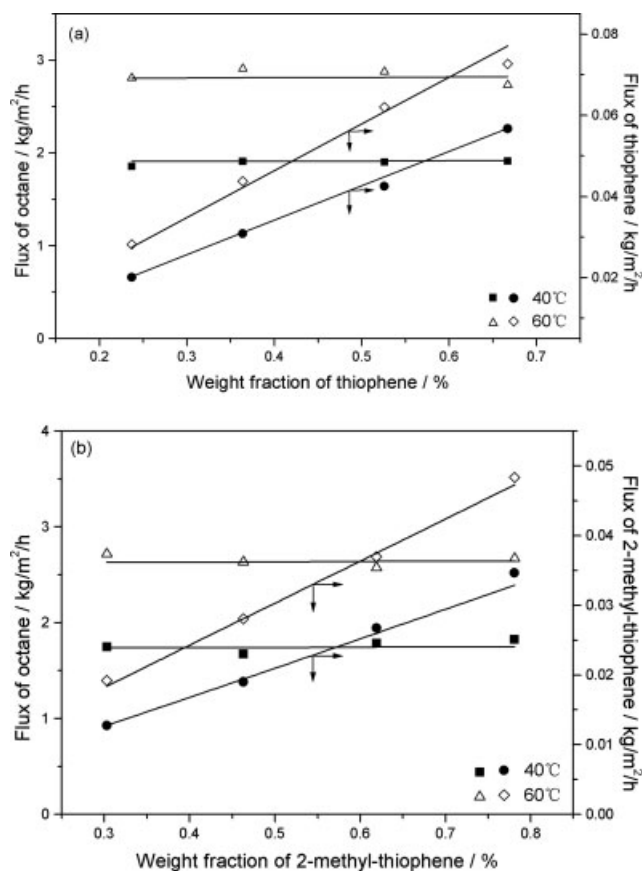


Figure 3 Effect of feed composition on partial flux for *n*-octane/thiophene (a) and *n*-octane/2-methyl-thiophene (b) mixture system at feed temperature 40 and 60°C. The curves are predicted with the solution-diffusion model. The symbols are the experimental data (■●; this work), (△◇).²²

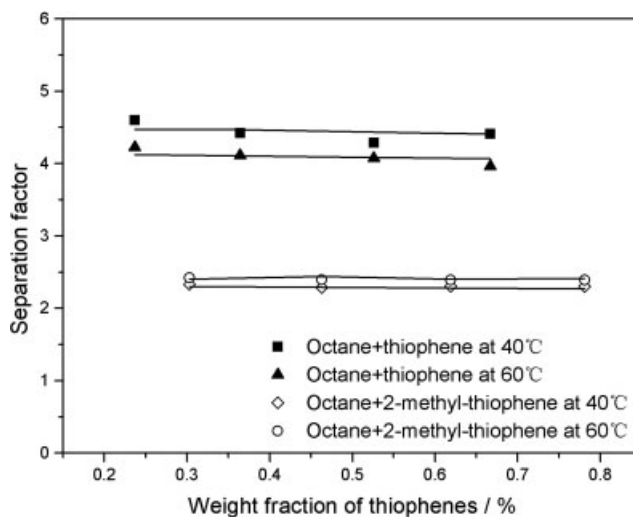


Figure 4 Effect of feed composition on selectivity for *n*-octane/thiophene and *n*-octane/2-methyl-thiophene mixture system at feed temperature 40 and 60°C. The curves are predicted with the solution-diffusion model. The symbols are the experimental data.²³

TABLE I
Antoine Constants for Various Penetrants^{19,20}

Component	A	B	C
<i>n</i> -Hexane	15.7476	2614.38	-46.58
<i>n</i> -Heptane	15.8737	2911.32	-56.51
<i>n</i> -Octane	15.9426	3120.29	-63.63
<i>n</i> -Nonane	15.9671	3291.45	-71.33
Thiophene	16.0243	2869.07	-51.80
2-Methyl-thiophene	4.84344	1812.350	-10.276

the feed side of the membrane cell by a pump with adjustable function of flow rate. High-feed flow rate up to 20 L/h and annular feed chamber are employed in the experiments to minimize the effect of concentration polarization on pervaporation performance. The feed solution is maintained at temperatures between 30 and 70°C using a thermostat (the precision degree is 0.1°C). Vacuum on the permeate side is maintained below 500 Pa and is monitored with a digital vacuumeter. Two cold traps, set in parallel and used alternatively, are applied to collect the permeate without rupture of the vacuum. The flux is determined by measuring the weight of permeate collected in the cold trap and divided by time and the membrane's surface area as shown in eq. (40).

$$J = \frac{m}{At} \quad (40)$$

where m denotes weight of the permeate passing through the effective membrane area A during the time t .

The compositions of the feed solution and permeate are analyzed by gas chromatography (HP6890, USA). Then the selectivity of a membrane in a binary system is obtained as follows:

$$\alpha_{ij} = \left(\frac{w_i^p}{w_j^p} \right) \left(\frac{w_j^f}{w_i^f} \right)^{-1} \quad (41)$$

where w^p and w^f refer to the weight fraction of penetrant i (thiophene or 2-methyl-thiophene) or j (alkane) in the permeate and in the feed, respectively.

RESULTS AND DISCUSSION

The experimental results for the concentration dependence of flux and selectivity for octane/thiophene and octane/2-methyl-thiophene mixtures in PDMS membrane system are presented in Figures 3 and 4.

As an application, the model presented in this work is used to predict the permeation fluxes and separation factors of alkane/thiophene and alkane/2-methyl-thiophene mixtures in PDMS membrane system. A new set of group interaction parameters are required to accurately predict the activity of penetrants in various polymer membrane systems. The parameters for the diffusion equation are fitted with the experimental data. The van der Waals volume and surface area parameters for the groups and the original group interaction parameters are taken directly from the Ref.¹⁸. The Antoine constants and the density parameters for the penetrants from literatures^{19,20} are listed in Table I and Table II. The required model parameters (a_{mk} , a_{km} , A_{iM} , B_{iM}) were determined by minimization of the following objective function using the Simplex-Nelder-Mead method.²¹

$$F(a_{mk}, a_{km}, A_{iM}, B_{iM}) = \sum_{np} \text{abs} \left(\frac{J_{\text{exp}} - J_{\text{cal}}}{J_{\text{exp}}} \right) = \min \quad (42)$$

where np is the number of data points. The obtained new interaction parameters between groups Si—O and thiophene (a_{mk} , a_{km}) and the diffusion coefficient parameters (A_{iM} , B_{iM}) which take into account the related systems are listed in Table III and Table IV, respectively.

The overall results for alkane/thiophene and alkane/2-methyl-thiophene mixtures in PDMS membrane system calculated by the solution-diffusion model proposed in this work are shown in Table IV and Figures 2–6. It can be seen from Table IV that the average mean relative deviations for the flux and separation factor of the two systems are 2.40% and 1.74%, respectively.

The temperature dependence of fluxes and selectivities for thiophene/*n*-octane and 2-methyl-thiophene/*n*-octane mixtures in PDMS system is

TABLE II
Density Parameters for Various Penetrants¹⁹

Equation	$\rho = M \times C_1/C_2^{(1-T/C_3)C_4}$ (kg/m ³)			
Penetrant	C_1 (kmol/m ³)	C_2	C_3 (K)	C_4
<i>n</i> -Hexane	0.70824	0.26411	507.6	0.27537
<i>n</i> -Heptane	0.61259	0.26211	540.2	0.28141
<i>n</i> -Octane	0.53731	0.26115	568.7	0.28034
<i>n</i> -Nonane	0.48387	0.26147	594.6	0.28281
Thiophene	1.2875	0.29185	579.35	0.3077
2-Methyl-thiophene	1.2565	0.3066	568.95	0.3175

TABLE III
New-Group Interaction Parameters between Si—O and Thiophene

Groups	Si—O	Thiophene
Si—O	0	107.40
Thiophene	129.85	0

illustrated in Figure 2. It can be seen from Figure 2 that the fluxes increase and the selectivities decrease with the increasing temperature and the fluxes and selectivities are higher in thiophene/*n*-octane system than those in 2-methyl-thiophene/*n*-octane system. The results show that the PDMS membrane is more selective to thiophene than to 2-methyl-thiophene, which will be significant for the desulfurization of gasoline. It can be found from Table IV and Figure 2 that the model works well in these systems.

Figures 3 and 4 show the effect of feed composition on partial flux and separation factor for *n*-octane/thiophene and *n*-octane/2-methyl-thiophene mixture system at feed temperature 40 and 60°C. It can be seen that variation of feed composition had nearly negligible influence on fluxes of octane and separation factor, whereas the partial fluxes of thiophenes are proportional to the concentrations of thiophenes in the feed. Under the same concentration in the two systems, the partial fluxes increase, whereas the separation factors decrease with the increasing temperature. It can be also seen that the predicted fluxes and selectivities in the two systems are in good agreement with the experimental data.

Figures 5 and 6 show the temperature dependence of partial fluxes and separation factors for different alkane/thiophene mixtures. It can be found that the partial fluxes increase with the feed temperature in all cases and partial fluxes of alkanes and thiophenes in different systems decrease, whereas the separation

factors increase with the increase of carbon number in the alkanes under the same temperature. This maybe explained by the fact that the coupling effect exists between the penetrants. The variation of penetrant *j* in the polymer membrane system may influence the solution and diffusion of penetrant *i*, so that different alkanes or thiophenes may affect the flux of the other penetrant. The results in these systems show that the PDMS membrane is easier to remove thiophene from nonane than from other three alkanes. As can be shown from Figures 5 and 6, the model performs well in these systems.

The results for the above systems show that the solution-diffusion model proposed in this article can be applied to predict the flux and selectivity of the pervaporation process. The temperature and concentration dependence of the flux and selectivity for the penetrants and the effect of different penetrants to the flux of the other penetrant in the membrane system can be depicted well by this model. The obtained results will be significant for the desulfurization process of gasoline which is mainly about removing of sulfur species such as thiophene and 2-methyl-thiophene from alkane mixtures.

CONCLUSIONS

In this article, a modified solution-diffusion model is proposed to account for the mass transport of penetrants in the polymer membrane. In the model, the group contribution method (the UNIFAC-ZM model) is first introduced to calculate the activity of penetrants in the polymer membrane, and a modified Fujita temperature-dependence diffusion coefficient equation is proposed to describe the diffusion behavior of the penetrants.

The permeation fluxes and separation factors of alkane/thiophene and alkane/2-methyl-thiophene mixtures in PDMS membrane system had been

TABLE IV
Diffusion Coefficient Parameters for the Penetrants in PDMS Membrane and Relative Deviations between Calculated Results and Experimental Values

System		$A_{Im} (\times 10^{-13})$	B_{iM}	Relative deviation (%)			
				Flux		Selectivity	
				Fujita	This work	Fujita	This work
<i>n</i> -Octane/2-methyl-thiophene	<i>n</i> -Octane	5.16	4.58	8.65	2.72	7.95	1.13
	2-methyl-thiophene	2.19	3.92	9.86	2.97		
<i>n</i> -Octane/thiophene	<i>n</i> -Octane	6.00	4.64	7.56	2.22	8.47	2.61
	Thiophene	3.23	3.61	8.43	3.46		
<i>n</i> -Hexane/thiophene	<i>n</i> -Hexane	10.67	4.02	6.74	0.85	9.38	2.13
	Thiophene	6.66	4.33	8.57	2.49		
<i>n</i> -Heptane/thiophene	<i>n</i> -Heptane	7.26	4.18	7.69	2.15	8.45	1.39
	Thiophene	3.42	3.73	9.58	2.53		
<i>n</i> -Nonane/thiophene	<i>n</i> -Nonane	4.58	5.14	8.25	2.82	7.53	1.45
	Thiophene	1.70	3.07	9.46	1.81		
Average				8.48	2.40	8.37	1.74

predicted with the proposed model. A good agreement between the calculated results and the experimental values is obtained, and the average mean relative deviations for the flux and separation factor of the two systems are 2.40% and 1.74%, respectively. The results are significant for desulfurization process of gasoline which mainly concerns removing sulfur species from alkanes. The solution-diffusion model proposed in this work can be applied to predict the effect of temperature and feed concentration on flux and selectivity of the pervaporation process with good accuracy. The parameters used in these systems can also be applied for the prediction of other systems.

Further improvement of the model and the prediction of flux and separation factor for other systems are in progress.

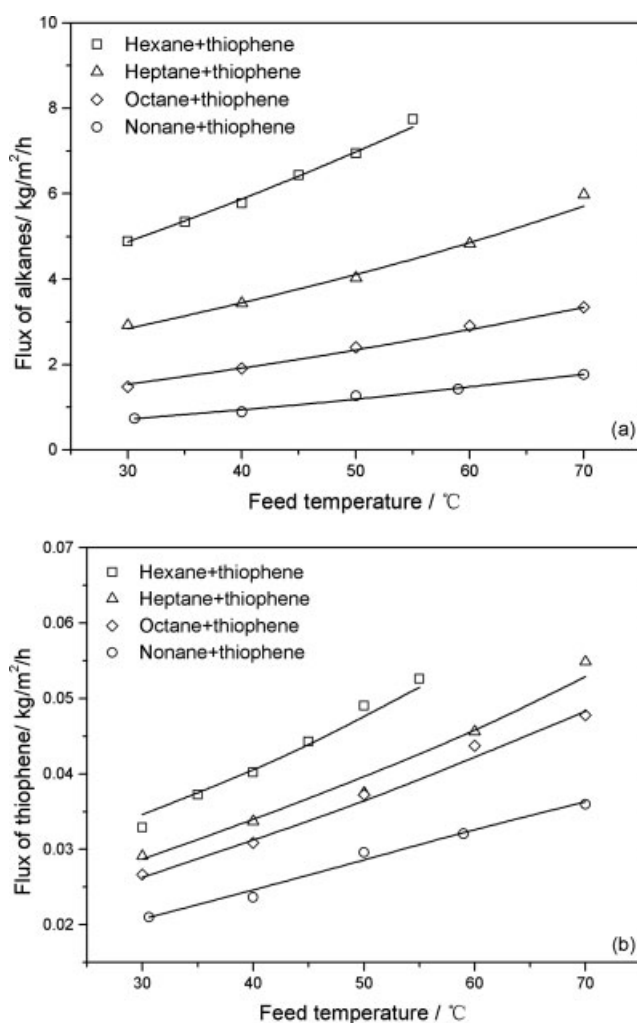


Figure 5 Temperature dependence of partial fluxes for different alkane/thiophene mixtures. System composition (wt %): *n*-hexane : thiophene = 99.57 : 0.43(□); *n*-heptane : thiophene = 99.58 : 0.42(△); *n*-octane : thiophene = 99.60 : 0.40(◇) and *n*-nonane/thiophene = 99.60 : 0.40(○). The curves are predicted with the solution-diffusion model. The symbols are the experimental data.²³

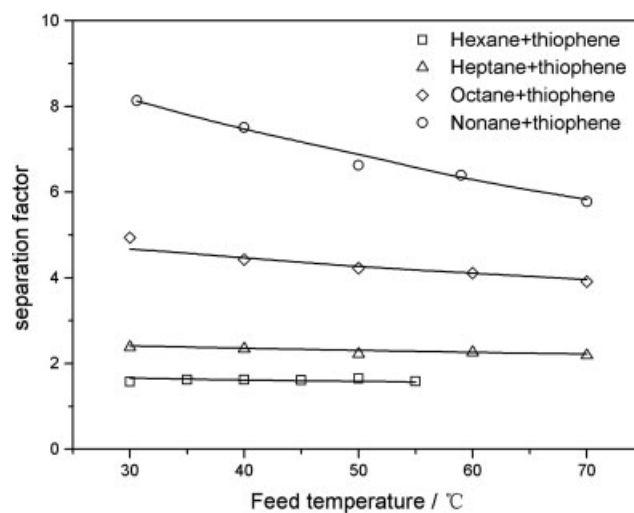


Figure 6 Temperature dependence of enrichment factor of thiophene for different alkane/thiophene mixtures. The curves are predicted with the solution-diffusion model. The symbols are the experimental data.²³

NOMENCLATURE

- a activity
- A_{di} free-volume parameters
- A_{iM} interaction parameter between penetrant and membrane
- B_d free-volume parameters
- B_{iM} interaction parameter between penetrant and membrane
- J_i partial flux of penetrant i ($\text{kg m}^{-2} \text{ h}^{-1}$)
- D_{iM}^* diffusion coefficient of penetrant i ($\text{m}^2 \text{ h}^{-1}$)
- c_i mass concentration of penetrant i (kg m^{-3})
- R general gas constant ($\text{J mol}^{-1} \text{ K}^{-1}$)
- T absolute temperature (K)
- x liquid phase mole fraction
- y vapor phase mole fraction
- V volume (m^3)
- P pressure (Pa)
- w_i weight fraction of component i
- $v_k^{(i)}$ the number of group k in molecular i
- $\tilde{f}_{p,i}$ fugacity
- Γ_k activity coefficient of group k at the mixture composition
- $\Gamma_k^{(i)}$ activity coefficient of group k at a group composition corresponding to pure component i
- Q_k group surface area parameter
- r volume parameter
- q surface area parameter
- Θ_m group surface area fraction of group m in the given system
- X_m mole fraction of group m in the given system
- a_{mk} group interaction parameter
- P_i^{sat} saturated vapor pressure (Pa)

Greek letters

α_{ij}	separation factor
$\beta(T)$	temperature dependent coefficient
ψ_{mk}	group interaction parameter
ϕ_i	volume fraction
θ_i	surface area fraction
μ	chemical potential
δ	thickness of the membrane (m)
γ	activity coefficient (mole fraction scale)
$\hat{\phi}_i$	fugacity coefficient

Superscripts

C	combinatorial part
res	residual part

References

1. Franke, M. Auslegung und Optimierung von Pervaporationsanlagen zur Entwässerung von Lösungsmitteln und Lösungsmittelgemischen, PhD Thesis, University of Aachen, Germany 1990.
2. Meyer-Blumenroth, U. Dampfpermeation. Untersuchungen zum Stofftransport und zur Verfahrensführung, PhD Thesis, University of Aachen, Germany, 1989.
3. Binning, R. C.; Lee, R. J.; Jennings, J. F.; Martin, E. C. *Ind Eng Chem* 1961, 53, 45.
4. Kedem, O. *J Membr Sci* 1989, 47, 277.
5. Stephan, W. Entwicklung eines Modells zum Stofftransport durch porenfreie Polymermembranen und Durchführung von Pervaporationsexperimenten, PhD Thesis, University of Heidelberg, Germany, 1993.
6. Okada, T.; Matsuura, T. *J Membr Sci* 1991, 59, 133.
7. Shieh, J. J.; Huang, R. Y. M. *Sep Sci Technol* 1998, 33, 767.
8. Graham, T. *Philos Mag J Sci* 1866, 32, 401.
9. Fels, M.; Huang, R. Y. M. *J Macromol Sci Phys* 1971, B5, 89.
10. Fujita, H. *Hochpolym Forsch* 1961, 3, 1.
11. Brun, J. P.; Larchet, C.; Melet, R.; Bulvestre, G. *J Membr Sci* 1985, 23, 257.
12. Huang, R. Y. M.; Shao, P.; Feng, X.; Anderson, W. A. *Ind Eng Chem Res* 2002, 41, 2957.
13. Schaetzel, P.; Vaclair, C.; Nguyen, Q. T.; Bouzerar, R. *J Membr Sci* 2005, 244, 117.
14. Wijmans, J. *J Membr Sci* 2004, 237, 39.
15. Peng, F.; Pan, F.; Li, D.; Jiang, Z. *Chem Eng J* 2005, 114, 123.
16. Cheng H. L. *J Appl Polym Sci* 1975, 19, 83.
17. Zhong, C.; Sato, Y.; Masuoka, H.; Chen, X. *Fluid Phase Equilib* 1996, 123, 97.
18. Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapour-Liquid Equilibria Using UNIFAC*. Amsterdam: Elsevier Science Publishers B V, 1977.
19. Perry, R. H.; Green, D. W.; Maloney, J. Q. *Physical and Chemical Data*, in: Perry's chemical engineers, handbook, 6th ed., New York: McGraw-Hill, 1984, p 7.
20. Eon, C.; Pommier, C.; Guiochon, G. *J Chem Eng Data* 1971, 16, 408.
21. Nelder, J. A.; Mead, R. *Comput J* 1965, 7, 308.
22. Qi, R.; Zhao, C.; Li, J.; Wang, Y.; Zhu, S. *J Membr Sci* 2006, 269, 94.
23. Qi, R.; Wang, Y.; Li, J.; Zhao, C.; Zhu, S. *J Membr Sci* 2006, 280, 545.