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Prediction of sorption and flux of solvents through PDMS membrane

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Abstract

Prediction method of permeation flux and sorption characteristics in pervaporation through a polydimethylsiloxane (PDMS) membrane was suggested. The amount of sorption and permeation flux of chloroform, toluene, methanol, and *n*-butanol were calculated using this method and compared with experimental data. The calculated values of permeation flux and the amount of sorption of good solvents, i.e. toluene and chloroform, were in fairly good agreement with the experimental data. The lower the density of PDMS membrane, the more the permeation flux and sorption quantity. However, the experimental data of poor solvents, i.e. methanol and *n*-butanol, were quite different from the calculated values. It is shown that the prediction method suggested in this study might be useful for predicting the sorption and permeation flux through the membrane. The prediction method might especially be helpful to design the pervaporation membrane system, as it does not need adjustable parameter or experimental data. © 2001 Published by Elsevier Science Ltd.

Keywords: Prediction; Sorption; Flux

1. Introduction

Membrane pervaporation is an engineering technology for the separation of many organic aqueous system; removal of organics from water, water removal from liquid organics, organic/organic separation, removal of volatile organic compounds (VOCs) from aqueous solution. Pervaporation transport can be described by the solution–diffusion model [1–3]. In the pervaporation process, one or more components in a liquid mixture preferentially absorbed on one side of a membrane, diffuse through the membrane matrix, and are desorbed and evaporated at the opposite membrane surface. This sequence of preferential sorption, diffusion, and evaporation is the basis for the separation of species by pervaporation. The different solubilities and diffusivities of the components in the membrane determine the membrane transport properties.

For the design of the membrane separation system, the experimental or predicted data on permeation flux through membrane should be available. Prediction method, which includes no adjustable parameters, is more useful to membrane system design. Provided that the permeation flux can be predicted only by the physical properties of membrane materials and solvents, it might be used for the membrane material design to separate/purify the specific mixtures properly or for selecting the system of mixtures to be purified/separated with specific membranes.

To predict the permeation flux, we need a prediction for both solubility and diffusivity. On the basis of the solution–diffusion model, the solubility and diffusivity of solvents in the membrane and membrane swelling determine the separation and transport properties for membranes. Several pervaporation models were proposed, and most of the models include adjustable parameters obtained from pervaporation, sorption, or diffusion experiments [4–6]. These prediction methods, including some adjustable parameters for the polymer or solvent, cannot be used for the design concept because the parameters must be determined by a diffusivity or solubility experiment.

In this study, a new membrane design concept is proposed. Since the permeation flux of each component in the mixture through membrane enables us to predict the membrane performance, the prediction of permeation flux is an important factor for pervaporation process design. The proposed prediction method does not include any adjustable parameters for the polymer or solvent. In other words, the proposed method can predict the permeation flux without any experiments. Especially, the suggested method predicts permeation flux using only the physical properties of membrane materials and solvents. As mentioned above, the estimation of the solubility and diffusivity of solvents

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Nomenclature

List of symbols

a_i	thermodynamic activity of component *i*
D	polymer/solvent binary mutual diffusion coefficient (cm^2/s)
D_0, D_1	constant pre-exponential factor (cm^2/s), solvent self-diffusion coefficient (cm^2/s)
E	energy required to overcome attractive forces from neighboring molecules (cal/mol)
ΔG	change in free energy relative to the standard state (J/kg)
ΔG_{el}, ΔG_{mix}	free energy of elastic deformation, free energy of mixing (J/kg)
K_{11}, K_{21}	solvent free-volume parameter (cm^3/g K), solvent free-volume parameter (K)
K_{12}, K_{22}	polymer free-volume parameter (cm^3/g K), polymer free-volume parameter (K)
n_{i}	the number of moles of component i
R	gas constant [1.987 cal/mol K]
T	temperature (K)
T_{g1}, T_{g2}	solvent glass transition temperature (K), polymer glass transition temperature (K)
$\hat{V}_i^*$	specific critical hole free volume of component *i* required for a jump (cm^3/g)
$\hat{V}_2^0$	specific volume of the pure polymer (cm^3/g)
$\hat{V}_{\mathrm{FH}i}$	specific hole free volume of pure component *i* at T
X	degree of cross linking

Greeks

μ_i	chemical potential of component *i*
μ_i^0	standard state chemical potential of component *i*
$\Delta\mu_{i,\mathrm{el}}$	the chemical potential changes of the solvents, in the network, due to elastic deformation
$\Delta\mu_{i,\mathrm{mix}}$	the chemical potential changes of the solvents, in the network, due to mixing
γ	overlap factor which accounts for shared free volume
l	membrane thickness (m)
ξ	ratio of critical molar volume of the solvent jumping unit to that of the polymer jumping unit
ϕ_i	volume fraction of component *i*
χ	Flory–Huggins polymer/solvent interaction parameter
w_i	mass fraction of component *i*

Superscripts

l	liquid phase on the feed side
m	polymer (membrane) phase

Subscripts

F	feed side
P	permeate side

in membrane matrix is needed for the prediction of permeation flux. For a solubility prediction, the UNIFAC-FV model [7] was used in this study. The Flory–Huggins equation and its modifications, however, frequently fail to predict the solubility of solvents in polymers because the interaction parameter, χ, is essentially empirical and adjustable. The solution–diffusion model assumes that swelling equilibrium is obtained by equating the chemical potential of the solvent in the bulk phase to the chemical potential of the solvent in the polymer phase. For a diffusion prediction, the free-volume theory proposed by Vrentas–Duda was employed because parameters of the free-volume theory for many types of polymer and solvent are already determined and Vrentas–Duda theory only enables us to predict diffusion coefficient of solvents in polymers. We can predict the solvent diffusivity in polymers without using any adjustable parameters obtained from the experiment.

Permeation flux depends on the driving force due to the solubility of solvent to membrane and diffusivity of solvent in membrane matrix. Using the predicted solubility and diffusivity in addition to the physical properties of membrane materials and solvents, the solubility of solvent to membrane, permeation flux and concentration in downstream at a given concentration in upstream are obtained and compared with other researchers' experimental data [4,5].

2. Theory

It is assumed that swelling equilibrium is reached at an interface between the feed liquid and swollen membrane. The concentration of solvents in the membrane interface was calculated from the thermodynamic chemical potential equilibrium relation.

Each component in the mixture diffuses through membrane matrix from the upstream side of interface to the downstream side of interface. The diffusion coefficient of each component is obtained. The diffusion coefficient was calculated using Vrentas–Duda's free volume theory and UNIFAC-FV method.

Using the predicted solubility and diffusivity in addition to the physical properties of membrane materials and solvent, the solubility of solvent to membrane, permeation flux and concentration in downstream at a given concentration in upstream are obtained.

2.1. Solubility of solvents to polymer membrane

As the solution–diffusion model assumes that swelling equilibrium is reached at an interface between the feed liquid and swollen membrane, the expression for swelling equilibrium is obtained by equating the chemical potential of the solvent in the bulk phase to the chemical potential of the solvent in the polymer phase [8]. The chemical potential at a given temperature and pressure can be obtained from the expression for the free energy.

$$\mu_i - \mu_i^0 = \frac{\partial(\Delta G)}{\partial n_i}, \tag{1}$$

where μ_i is the chemical potential of the solvent (component i), μ_i^0 is the standard state chemical potential of the solvent, ΔG is the change in free energy relative to the standard state, and n_i is the number of moles of solvent. To obtain an expression for ΔG the Flory–Rehner assumption of the separability of the free energy into the free energy of elastic deformation, ΔG_{el}, and the free energy of mixing, ΔG_{mix}, is often made [9–11], leading to the following:

$$\begin{aligned}\mu_i - \mu_i^0 = \Delta\mu_i^{\mathrm{m}} &= \frac{\partial(\Delta G_{\mathrm{el}})}{\partial n_i} + \frac{\partial(\Delta G_{\mathrm{mix}})}{\partial n_i} \\ &= \Delta\mu_{i,\mathrm{el}} + \Delta\mu_{i,\mathrm{mix}},\end{aligned} \tag{2}$$

where $\Delta\mu_{i,\mathrm{el}}$ and $\Delta\mu_{i,\mathrm{mix}}$ are the chemical potential changes of the solvents in the network due to elastic deformation and mixing, respectively.

The condition for the thermodynamic phase equilibrium between a liquid or gaseous mixture and the membrane swollen in this mixture is the equality of the chemical potential $\Delta\mu_i$ in both phases for each component i:

$$\mu_i^{\mathrm{l}} = \mu_i^{\mathrm{m}}. \tag{3}$$

With $\mu_i = \mu_i^0 + \mathrm{RT}\ln a_i$, Eq. (3) can be expressed with the activities a_i:

$$a_i^{\mathrm{l}} = a_i^{\mathrm{m}}, \tag{4}$$

where, superscripts l and m mean liquid phase and polymer (membrane) phase, respectively. In order to calculate the sorption of solvent at the membrane interface in this study, the activity of solvent in feed phase (a_i^{l}) in Eq. (4) was calculated from the given feed composition and temperature by use of UNIFAC [12]. As $a_i^{\mathrm{l}} = a_i^{\mathrm{m}}$ from swelling equilibrium, we can also determine the volume fraction of the solvent absorbed at the membrane interface of feed side ($\phi_{i,\mathrm{f}}$). The volume fraction of solvent ($\phi_{i,\mathrm{f}}$) absorbed at membrane interface of feed side was determined by least-square minimization, which is minimization of the objective function, $\sum(a_i^{\mathrm{l}} - a_i^{\mathrm{m}})^2$. The activity of solvent at membrane interface (a_i^{m}) using UNIFAC-FV was suggested by Ohishi–Prausnitz [7].

2.2. Solvent diffusion through polymer membrane matrix

In the free-volume theory of transport developed by Vrentas–Duda, solvent self-diffusion coefficient in cross linked polymer, D_1, for a polymer-penetrant mixture can be determined using the following equations [13]:

$$D_1 = D_0 \exp\left[\frac{-E}{\mathrm{RT}}\right]\exp\left[-\frac{w_1\hat{V}_1^* + w_2\xi\hat{V}_2^*}{w_1(\hat{V}_{\mathrm{FH1}}/\gamma) + w_2 f_2\delta}\right], \tag{5}$$

$$f_2 = \frac{\hat{V}_{\mathrm{FH2}}(T,0)}{\gamma}. \tag{6}$$

Here, w_i is the mass fraction of component i, $\hat{V}_i^*$ is the specific critical hole free volume of component i required for a jump, ξ is the ratio of the critical molar volume of the solvent jumping unit to the critical molar volume of the polymer jumping unit, D_0 is a constant preexponential factor, E is the energy per mole that a molecule needs to overcome attractive forces that hold it to its neighbors, T is the temperature, R is the gas constant, $\hat{V}_{\mathrm{FH}i}$ is the specific hole free volume of pure component i at T, γ is an overlap factor introduced because the same free volume is available to more than one molecule, and f_2 simply refers to the free-volume properties of the uncross linked polymer. The introduction of cross linking into the polymer will affect D_1 only through the quantity $\hat{V}_{\mathrm{FH2}}$. The volumetric relationships, which take into account the degree of cross linking, are as follows [13].

$$\delta = \frac{\hat{V}_{\mathrm{FH2}}(T,X)}{\hat{V}_{\mathrm{FH2}}(T,0)} = \frac{\hat{V}_2^0(0,X)}{\hat{V}_2^0(0,0)} = \frac{\hat{V}_2^0(T,X)}{\hat{V}_2^0(T,0)}, \tag{7}$$

where, $\hat{V}_2^0(T,X)$ is the specific volume of the pure polymer at a particular temperature T and a prescribed degree of cross linking as denoted by X. Parameter δ, which characterizes the effect of the cross linking on the free volume of the polymer, can be determined directly using volumetric data on the cross linked and uncross linked polymer. When

$\delta = 1$, Eq. (5) reduces to the result for solvent self-diffusion in an uncross linked polymer [14,15].

Since mutual diffusion coefficient (D) is useful for analyzing actual mass transfer phenomena in polymer/solvent system, self-diffusion coefficient (D_1) must be related to the binary mutual diffusion coefficient (D). Bearman [16] proposed the relationship between D and D_1 as follows:

$$D = \left(\frac{D_1 w_1}{\mathrm{RT}}\right)(1 - w_1)\left(\frac{\partial \mu_1}{\partial w_1}\right)_{T,P}. \tag{8}$$

For relating D_1 to D as shown in Eq. (8), derivative of solvent chemical potential (third term on the right hand side, i.e. $(\partial \mu_1/\partial w_1)_{T,P}$) must be obtained. The chemical potential derivative represents the effects of thermodynamic changes on the diffusion coefficient. Vrentas–Duda obtained the derivative of chemical potential (i.e. $(\partial \mu_1/\partial w_1)_{T,P}$) from the Flory–Huggins equation under the assumption of constant χ (binary interaction parameter).

However, the authors suggested new models in a previous paper [17], in which we derived the derivative of chemical potential (i.e. $(\partial \mu_1/\partial w_1)_{T,P}$) from the thermodynamic relation and calculated using UNIFAC-FV without any assumptions or simplification. In this work, we used the model suggested in a previous paper [17] for the prediction of mutual diffusion coefficient (D), which do not contain Flory–Huggins interaction parameter χ and do not include experimentally adjustable parameters.

2.3. Permeation flux

Stern [18] suggested that the permeation flux of component i can be expressed with the local volume fraction of component i in the polymer, ϕ_i, and the mutual diffusion coefficient, D.

$$J_\mathrm{i} = \frac{1}{l}\int_{\phi_{i,\mathrm{p}}}^{\phi_{i,\mathrm{f}}} \frac{D}{1 - \phi_i}\mathrm{d}\phi_i, \tag{9}$$

where J_i is the permeation flux of component i, l is the membrane thickness, $\phi_{i,\mathrm{f}}$ and $\phi_{i,\mathrm{p}}$ are volume fraction of solvent at feed side membrane interface and at permeate side membrane interface, respectively. When the pressure in permeate side is sufficiently low, $\phi_{i,\mathrm{p}}$ becomes zero. Therefore, using $\phi_{i,\mathrm{f}}$ determined by swelling equilibrium and D calculated by using UNIFAC-FV, we can predict the permeation flux.

During the permeation, the membrane thickness l varies because of swelling. Therefore, to calculate the membrane thickness variation, the dimensionless t can be expressed as:

$$t = \frac{x}{l} = \frac{\displaystyle\int_{\phi_x}^{\phi_{i,\mathrm{f}}} \frac{D}{1 - \phi_i}\mathrm{d}\phi_i}{\displaystyle\int_{\phi_{i,\mathrm{p}}}^{\phi_{i,\mathrm{f}}} \frac{D}{1 - \phi_i}\mathrm{d}\phi_i} \qquad (0 < t < 1). \tag{10}$$

If isotropic swelling is assumed, the following relationship is obtained [19].

$$\mathrm{d}l = \frac{1}{\phi_\mathrm{p}^{1/3}}\mathrm{d}l_\mathrm{d}, \tag{11}$$

where, ϕ_p is the volume fraction of the polymer. l_d and l are the thickness of the original dry membrane and the swollen membrane, respectively. By introducing the dimensionless t into Eq. (11) the following equation was obtained.

$$\frac{l_\mathrm{d}}{l} = \int_0^1 \phi_\mathrm{p}^{1/3}\mathrm{d}t \tag{12}$$

From Eqs. (10) and (12), swollen membrane thickness with absorbed solvent can be obtained.

3. Results and discussion

3.1. Method of solution

For a given feed composition and given vacuum side pressure of zero in PDMS/solvent system, the concentration of solvent at the membrane interface of feed side, mutual diffusion coefficient of solvent in the membrane and permeation fluxes is calculated. The following procedures are used to solve the problem.

1. The activities in the feed phase (a_i^l) in Eq. (4) are first calculated from the given feed composition and temperature using of UNIFAC [12].
2. As $a_i^\mathrm{l} = a_i^\mathrm{m}$ from swelling equilibrium, the concentration of solvents at the membrane interface of feed side ($\phi_{i,\mathrm{f}}$) according to the given feed composition and temperature can be determined by using UNIFAC-FV and least-square minimization, which is minimization of the objective function, $\sum(a_i^\mathrm{l} - a_i^\mathrm{m})^2$.
3. Mutual diffusion coefficients of solvents in the polymer membrane are calculated using Eqs. (5)–(8). The derivative term (i.e. $(\partial \mu_1/\partial w_1)_{T,P}$) of Eq. (8) is determined by use of UNIFAC-FV without any assumptions or simplification.
4. Permeation fluxes of solvent through the membrane are calculated using the calculated mutual diffusion coefficient (D) and the sorption of solvent at the membrane interface ($\phi_{i,\mathrm{f}}$). Eq. (9) proposed by Stern [18] is used to calculate the permeation flux. Also, Eqs. (10) and (12) are used to consider the membrane thickness (l) variation due to swelling.

In the estimation of the solvent solubility into the membrane, elastic deformation makes only a small contribution for change in chemical potential. The chemical potential change due to elastic deformation is considered negligible in comparison with the chemical potential change due to mixing [20]. Values of the density for amorphous PDMS polymer [21] were used for calculating δ, which is

Table 1
Parameters used in diffusion coefficient predictions of solvents in PDMS

Parameters[a]	Chloroform /PDMS system	Methanol /PDMS system	Toluene /PDMS system
$\hat{V}_1^*$ (cm^3/g)	0.51	0.961	0.917
$\hat{V}_2^*$ (cm^3/g)	0.905	0.905	0.905
$K_{11}/\gamma \times 10^3$ (cm^3/g K)	0.71	1.17	1.15
$K_{12}/\gamma \times 10^4$ (cm^3/g K)	9.32	9.32	9.32
$K_{21} - T_{g1}$ (K)	−29.43	−48.41	−102.72
$K_{22} - T_{g2}$ (K)	−81	−81	−81
$\alpha^b \times 10^3$	15.87	15.87	15.87
ξ	0.9662	0.4887	1.341
$D_o \times 10^4$ (cm^2/s)	4.07	8.75	1.87
E (cal/mol)	0	0	0

[a] Hong [14].

[b] Hong [24].

used for estimating the self-diffusivity. To determine the permeation flux and sorption characteristics, the density values of PDMS reported by Yoo et al. [22] were used. In spite of the same polymer, the density of polymer varies with molecular weight, crystallinity and degree of cross linking of the polymer. We predicted the sorption characteristics and the permeation fluxes using the densities (1.1115, 1.1293, 1.1345, 1.1507) according to the hardness of the cross linked PDMSs reported by Yoo et al. [22]. Free-volume parameters used for the prediction of mutual diffusion coefficient of solvent in the PDMS membrane are listed in Table 1. Various methods for calculating each free volume parameter of polymers and solvents are presented by Zielinski et al. [15] and Hong [14].

The PDMS membrane used in this study is a hydrophobic polymer and the amount of water sorption into the PDMS membrane is very little. Therefore, as the sorption of good solvent from an aqueous mixture into PDMS can be considered as binary system, this study considers the feed phase as a binary system of water/solvent and the membrane phase as a binary system of solvent/PDMS polymer [4].

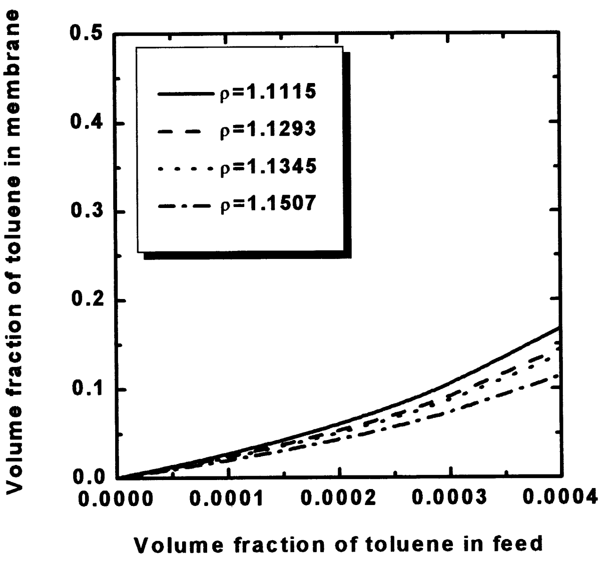

Fig. 1. Theoretical predictions for sorption of toluene in PDMS at 30°C.

Polymer is swollen by sorption of solvent and the swelling changes the thickness of membrane. Membrane thickness is used to determine the permeation flux. In this study, the changes of membrane thickness during permeation was considered using Eqs. (10) and (12).

3.2. Sorption and permeation flux of good solvents (toluene, chloroform) to PDMS membrane

Predicted results of sorption and permeation flux of good solvents (toluene, chloroform) to PDMS membrane were compared with experimental data as shown in Figs. 2, 3, and 5.

3.2.1. Sorption of toluene to PDMS membrane

For a given volume fraction of toluene in feed solution (water/toluene), sorption of toluene into PDMS membrane was calculated by swelling equilibrium. The calculated volume fractions of toluene at the membrane interface of feed side are shown in Fig. 1. The sorption of toluene increased with increase in feed side concentration of toluene, and decreased with increase in membrane density.

3.2.2. Permeation flux of toluene through PDMS membrane

The calculated volume fraction of toluene at the membrane interface of feed side was used for the estimation of permeation flux of toluene through PDMS membrane. The calculated permeation fluxes of toluene at various volume fractions of toluene in feed solution are shown in Fig. 2. Permeation fluxes were increased with increasing toluene concentration in feed solution. Increase in membrane density brought about decrease in permeation flux of toluene through PDMS membrane. The calculated values in case of toluene (toluene is one of the good solvents which promotes polymer swelling) fit fairly well with the experimental results [5].

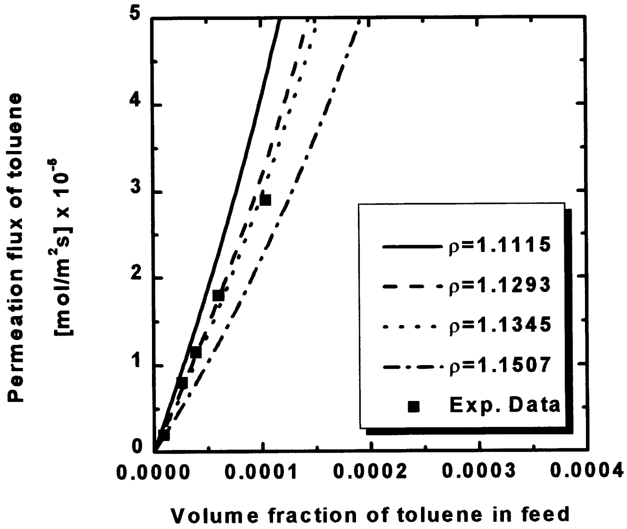

Fig. 2. Experimental data [5] and theoretical predictions for flux of toluene in PDMS at 30°C.

3.2.3. Sorption of chloroform to PDMS membrane

Activity of chloroform in feed solution (chloroform/water) was calculated with UNIFAC method and is shown in Fig. 4. Activity of chloroform in PDMS membrane was calculated by use of UNIFAC-FV method at various sorptions of chloroform into PDMS membrane. The calculated values and experimental data [4] are shown in Fig. 3. The prediction is successful to some degree, especially in the lower solvent fraction region. Solubility of chloroform into PDMS increases with decreasing membrane density. In other words, the concentration of chloroform at the membrane interface increases with decreasing density, which means that less membrane density is good for enhancing the permeation flux. Using Figs. 3 and 4, we can determine the concentration of chloroform in feed solution.

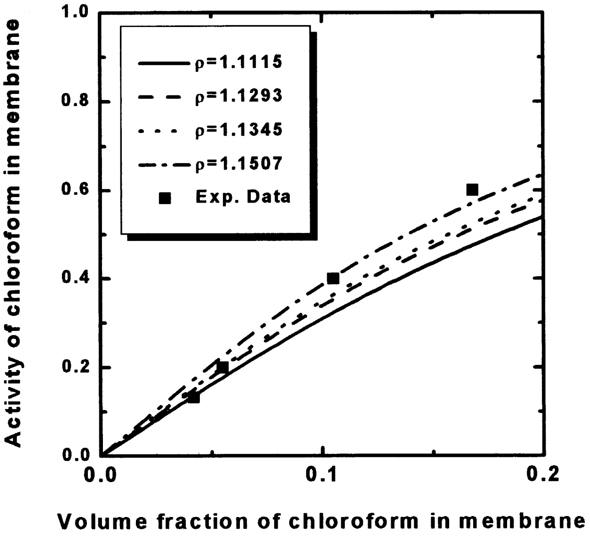

Fig. 3. Experimental data [4] and theoretical predictions for sorption of chloroform in PDMS at 40°C.

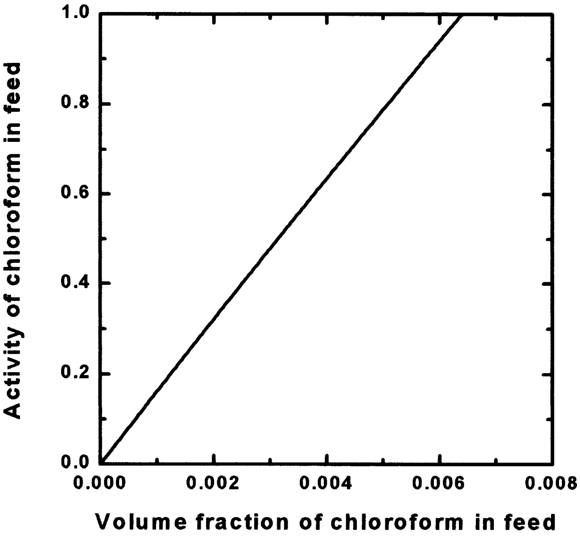

Fig. 4. Theoretical prediction using UNIFAC for activity of chloroform in feed (chloroform + water system) at 40°C.

3.2.4. Permeation flux of chloroform through PDMS membrane

Permeation flux through the PDMS membrane at various volume fractions of chloroform in the membrane is shown in Fig. 5. More sorption of chloroform into PDMS membrane increases the driving force for the diffusion of chloroform through the membrane matrix. Therefore, the permeation flux increases with the more sorption into PDMS membrane. It also shows that less membrane density results in more permeation flux. In the range of higher volume fractions of chloroform in membrane, the calculated values and experimental data on permeation flux are not in so good agreement. In lower concentration range, however, the calculated values and experimental data agree well. As pervaporation processes are usually applied

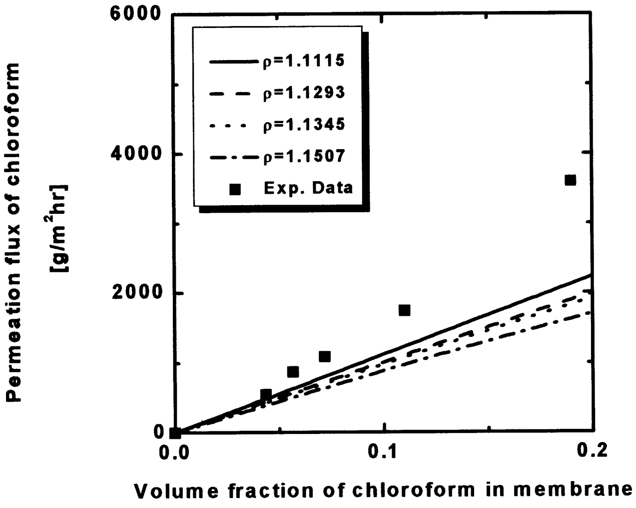

Fig. 5. Experimental data [4] and theoretical predictions for flux of chloroform in PDMS at 40°C.

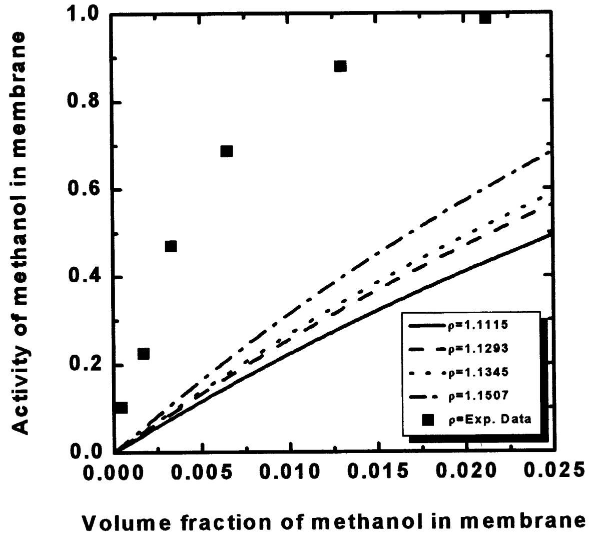

Fig. 6. Experimental data [4] and theoretical predictions for sorption of methanol in PDMS at 40°C.

for the separation of solvent from very dilute aqueous solution, this calculation method is meaningful for predicting the permeation flux in pervaporation processes.

3.3. Sorption and permeation flux of poor solvents (methanol, n-butanol) to PDMS membrane

Sorption characteristics and permeation flux of poor solvents (methanol and *n*-butanol; a kind of the poor solvent which does not promote polymer swelling) were predicted. The predicted values were compared with the experimental data reported by Favre et al. [4].

3.3.1. Sorption of methanol to PDMS membrane

For a given volume fraction of methanol at the membrane interface on the feed side, the activity of methanol in PDMS membrane matrix was calculated using UNIFAC-FV. The calculated activity of methanol at the membrane interface on the feed side was shown in Fig. 6. For a given volume fraction of methanol in feed solution (water/methanol), activity of methanol in feed solution was calculated and shown in Fig. 7. Sorption of methanol (poor solvent) into PDMS membrane is much smaller than that of a good solvent even at relatively high concentration of methanol as shown in Figs. 6 and 7. From Fig. 6 we can see that the difference between predicted values and experimental data of sorption becomes larger as the concentration of sorbed solvent becomes higher. It seems that the suggested prediction method in this study may not deal with the poor solvent. In case of poor solvents, the results were similar to the report of Favre et al. [4]. They used the Koningsveld and Kleinjtens equation [4,23] because the Flory–Huggins equation caused a large error.

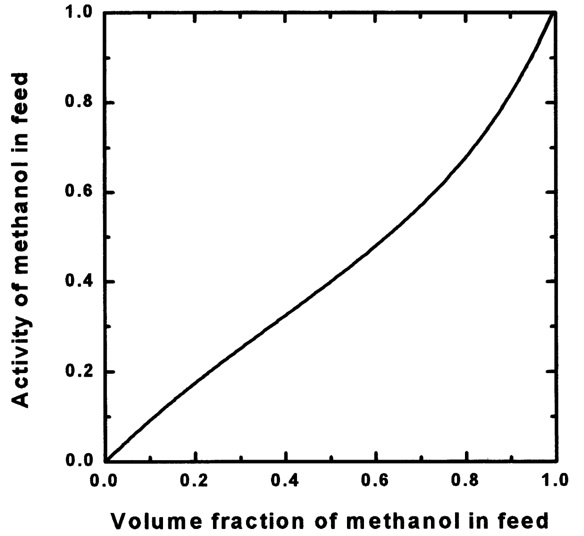

Fig. 7. Theoretical prediction using UNIFAC for activity of methanol in feed (methanol + water system) at 40°C.

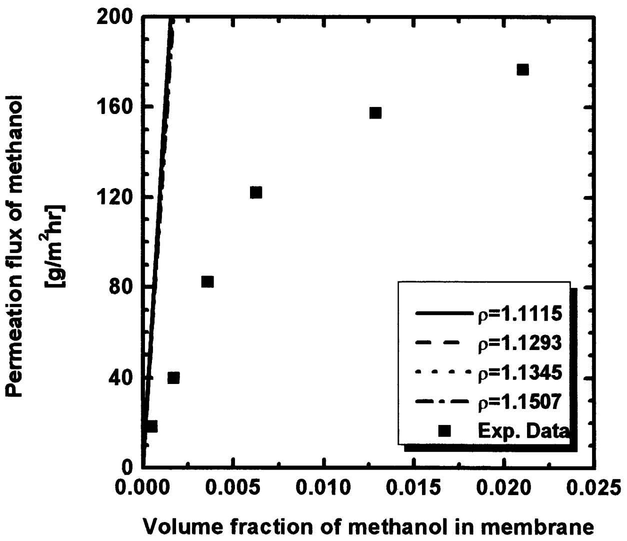

Fig. 8. Experimental data [4] and theoretical predictions for flux of methanol in PDMS at 40°C.

3.3.2. Permeation flux of methanol through PDMS membrane

Calculated and experimental data on permeation flux of methanol through PDMS membrane at membrane interface on the feed side are shown in Fig. 8. The calculated values (methanol is one of the poor solvents) were quite different from the experimental results. The difference became larger as the volume fraction of methanol in the membrane interface increased. It seems that the suggested prediction method in this study may not deal with the methanol (poor solvent).

3.3.3. Sorption of n-butanol to PDMS membrane

For a given volume fraction of *n*-butanol (poor solvent) at the membrane interface, the activity of *n*-butanol in PDMS membrane is shown in Fig. 9. Similar to the case

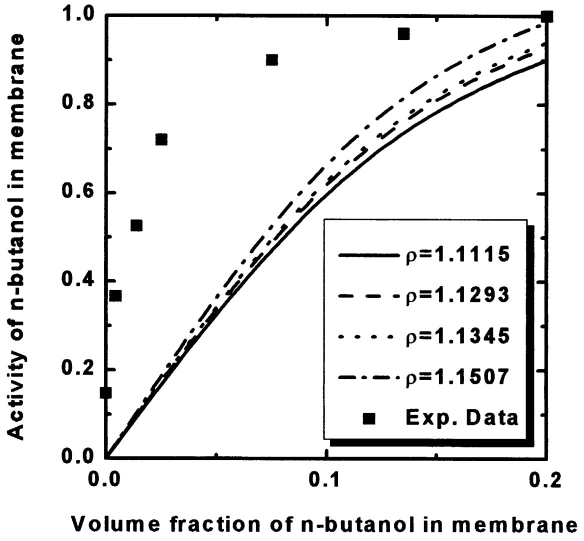

Fig. 9. Experimental data [4] and theoretical predictions for sorption of *n*-butanol in PDMS at 40°C.

of methanol, the calculated values were quite different from the experimental results. It seems that the suggested prediction method in this study may not deal with *n*-butanol (poor solvent). Fig. 9 shows that the sorption of *n*-butanol to PDMS membrane was greater than that of methanol (Fig. 6).

3.3.4. Discussion on the difference between predicted and experimetal values

Figs. 2, 5 and 8 show that the differences between calculated values and experimental data become larger as the concentration of solvent increases. One of the reasons might be that the Eq. (8), which relates the self-diffusion coefficient (D_1) to the mutual diffusion coefficient (D), is valid in the range of low concentration. Another might be that the density of membrane depends on the degree of the cross linking of polymer and the density affects the sorption and permeation flux. The effect of such reasons is much more serious for poor solvents than good solvents.

4. Conclusions

Prediction method of the sorption and permeation flux through PDMS membrane was proposed and the calculated values and experimental data were compared. For good solvents (toluene, chloroform), the calculated values were in fairly good agreement with the experimental data, especially in a low range of feed concentration. However, there was some difference between the calculated and experimental data for poor solvent (methanol, *n*-butanol). The suggested prediction method might be useful for predicting the sorption and permeation flux through membranes. The prediction method might be particularly helpful to the design of pervaporation membrane systems, since the suggested method does not need adjustable parameter or experimental data.

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