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# Prediction of solvent solubility, diffusivity and permeability in glassy polymeric membranes

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**Abstract**

The filling-type membrane is composed of grafted polymer and solvent resistant substrate; calculation of solubility, diffusivity and the swelling-suppression effect of a substrate enabled us to predict solvent permeability. This approach, noted as membrane design, has previously been used in estimating permeability of aromatic compounds through rubbery polymeric membranes. In this study, the influence of plasticization on solubility and diffusivity is investigated theoretically and experimentally with poly(methyl methacrylate) (PMMA). Solubilities predicted by a group-contribution lattice-fluid equation of state (GCLF-EOS) model are consistent with the results of vapor sorption. A modified free volume model is proposed for calculating solvent diffusion in glassy polymers by taking into account the compositional dependence of depression on the glass transition temperature. The solvent diffusion coefficient has a clear transformation at an isothermal glass transition concentration, and predictions are consistent with those measured by vapor permeation. Fluxes of benzene and toluene through filling-type PMMA membrane are measured by vapor permeation experiments, and it was found that the predictions agreed with the experiments. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords*: Glassy polymer; Membrane design; Diffusion coefficient

## 1. Introduction

During the past decade, membrane separation has been demonstrated as a promising unit operation technique offering specific merits over many conventional separation processes, such as recovery of organics from emission and purification of solvents, thus increasing the need for membranes with excellent separation properties. Development of novel membranes is, however, still time-consuming and high cost work because of a lack of design methodology.

In general, a solution–diffusion mechanism can describe solvent permeation through non-porous polymer membranes [1,2]. Solubility and diffusivity dominate the permeability of molecule through membranes. Many mathematical models have been proposed to simulate this process [3–5], and significant progress has recently been made by closely incorporating penetration with molecular configuration [6,7]. Each of these models, however, includes one or more fitting parameters determined from solvent sorption or permeation measurements. This approach gives rise to a loss of predictive power, although such an approach is effective in some situations.

Physical properties of polymer solutions are closely associated with polymer morphology and its change with environmental conditions, e.g. temperature and solvent composition. Extensive research on the physical properties of polymers can benefit in the development of membrane design methods. Using this conceptual framework, polymer physical properties connect polymer science and its application to membrane separation, and make it possible to predict the separation performance without any data from direct measurements of a membrane.

On the basis of widely collected data on the permeability of gases through various glassy polymer membranes, and using these experimental results to determine the group contribution for permeability, models were developed to predict permselectivity of other polymeric structures with a group-contribution approach [8–10]. Although these models successfully predicted membrane performances for gas separation, they suffer from the limitation of being applicable to only a few gases.

Apart from the above approach, we have previously developed a methodology for designing a filling-type membrane [11], which is composed of two materials: a

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**Nomenclature**

| | |
|---|---|
| $A$ | grafted polymer fraction in grafted membrane equal to 0.81 |
| $a_1^{\mathrm{pure}}$ | solvent activity in pure polymer |
| $a_1^{\mathrm{ss}}$ | contribution of substrate swelling-suppression effect |
| $a_1^{\mathrm{m}}$ | solvent activity in filling-type membrane |
| $f$ | elastic factor of substrate |
| $J_1$ | solvent flux, kg/m$^2$ h |
| $l$ | membrane thickness, mm |
| $L\langle v_{\mathrm{m1}}\rangle$ | dimensionless membrane thickness |
| $K_{ij}$ | free volume parameters |
| $\tilde{P}$ | reduced pressure |
| $q_1$, $q$ | effective chain length or surface area parameter for a component or a mixture, respectively |
| $r$ | number of lattice sites for a mixture |
| R | gas constant, J/kmol K |
| $\tilde{T}$ | reduced temperature |
| $T$ | operating temperature, K |
| $T_{\mathrm{g2}}$ | glass transition temperature of pure polymer, K |
| $T_{\mathrm{gm}}$ | glass transition temperature of polymer mixture, K |
| $T_{\mathrm{m}}$ | substrate polymer melt temperature, K |
| $v_1$ | solvent volume fraction |
| $\tilde{v}_1$ | reduced volume fraction of solvent |
| $V_1^*$, $V_2^*$ | specific hole free volume of solvent and polymer required for a diffusion jump, cm$^3$/g |
| $w_1$, $w_2$ | mass fraction of solvent and polymer |
| $z$ | lattice coordination number equal to 10 |
| *Greek letters* | |
| $\beta$ | plasticization factor |
| $\gamma$ | overlap parameter which accounts for shared free volume |
| $\Gamma_{11}$ | non-randomness parameter |
| $\Delta H_{\mathrm{sub}}$ | molar heat of fusion of polyethylene crystal, cal/mol |
| $\theta$ | molecule surface fraction of a mixture |
| $\xi$ | ratio of the critical molar volume of the solvent jumping unit to that of the polymer jumping unit |
| $\phi_1$ | solvent volume fraction in a mixture |
| $\chi$ | intermolecular interaction parameter |

porous substrate and a grafted polymer that fills the pores of the substrate. This membrane is suitable for separating organic mixtures [12,13]. Membrane materials and the mechanical strength of the substrate can be chosen solely by calculation, provided solvent solubility and diffusivity in the filling polymer and the swelling-suppression effect of the substrate can be quantitatively estimated. This approach has been previously employed to design membranes for volatile organic compound (VOC) removal [11,14], and has been recently extended to predict the permeability of associated solvent systems (e.g. hydrogen bonding) [15]. Nevertheless, we have observed with the present model, that the calculation of solvent permeation through glassy polymeric membranes obviously deviates from experimental results. Such deviations occur, for example, for solvent plasticization, which changes the polymer configuration and affects penetration behavior. In fact, permeation of organic solvent through a glassy polymeric membrane is commonly used in several industrial processes. Due to the complexity of molecular diffusion in a glassy polymer, few models have been fully developed to describe penetration behavior. This has motivated us to investigate solubility and diffusivity in glassy polymers, taking into account the effect of solvent plasticization. These results will be useful for perfecting our membrane design method.

In this paper, we extend our approach of membrane design to glassy polymer membranes by investigating solvent solubility and diffusivity around the glass transition point, taking into account solvent plasticization. Measurements on solubility were compared with those predicted from the group-contribution lattice-fluid equation of state (GCLF-EOS) model. A modified free volume theory proposed in our previous study [16] was adopted to predict solvent diffusivity for glassy polymer mixtures, and evaluated in the light of experimental results. Finally, solvent fluxes (benzene and toluene) were measured through poly(methyl methacrylate) (PMMA) filling-type membranes with vapor permeation experiments under various operating conditions.

## 2. Theory

### 2.1. Isothermal glass transition

It is well known that sorption of organic vapor by polymers yields plasticization, resulting in significant depression of the glass transition temperature. In other words, a glassy polymer isothermally changes into a rubbery state only by sorption of vapor. Using classical thermodynamic theory, the glass transition temperature of the solvent and polymer mixture can be described by the following equation [17]:

$$T_{\mathrm{gm}} = \frac{x_1 \Delta C_{p1} T_{\mathrm{g1}} + x_2 \Delta C_{p2} T_{\mathrm{g2}}}{x_1 \Delta C_{p1} + x_2 \Delta C_{p2}} \tag{1}$$

where the subscripts 1 and 2 denote solvent and polymer, respectively, $T_{gi}$ is the glass transition temperature of the pure components, and $\Delta C_{pi}$ represents the incremental change in heat capacity at $T_{gi}$. Most values of solvent glass transition have been published from free volume theory [18]. The mole fraction, $x_i$, can be calculated using the molecular weight of the repeat unit for polymers.

Table 1 shows the characteristic properties used in this work. The incremental change of heat capacity for solvent at $T_{\mathrm{g1}}$, for benzene and toluene, was obtained by regressing

Table 1
Pure component specific property

| Component | $T_g$ (K) | $\Delta C_p$ (J/g K) | Ref. |
|---|---|---|---|
| Benzene | 131 | 0.52 | – |
| Toluene | 117 | 0.60 | – |
| PMMA | 378 | 0.33 | [20] |

experimental data [19] of benzene/polystyrene and toluene/polystyrene systems with Eq. (1). For other polymers, these parameters are available.

### 2.2. Solubility

In general, glassy polymer mixtures are regarded as a non-equilibrium liquid, and a dual-mode model is widely adopted for describing sorption behavior of gases like carbon dioxide and nitrogen. Specifically, sorption is considered to have both equilibrium (Henry's) and non-equilibrium (Langmuir's) contributions, and three fitting parameters are used in the calculations. Unlike the situation in gas sorption, due to the significant effect of solvent plasticization, the non-equilibrium sorption term largely decreases, and the equilibrium part almost dominates this process. For this reason, sorption isotherm in a glassy polymer and solvent system often takes on the shape that a rubber polymer possesses. Thermodynamic theory, developed to predict phase behavior for equilibrium polymer solutions, might provide acceptable estimates of solubility in the glassy states.

Solubility is a prerequisite condition for solvent penetration through polymeric membranes. Although many models have been summarized [21,22], the GCLF-EOS model [23] has some advantages over others, and its reliability has been compared, in our previous study [14], with the UNIFAC-FV model. The result of the GCLF-EOS model encourages us to adopt it for glassy polymers. The GCLF-EOS model was developed to predict phase behavior of equilibrium polymer solutions [23], and it will now be extrapolated to the non-equilibrium range below the glass transition point by taking account of solvent plasticization. Solvent solubility can be calculated from the following expression:

$$\frac{\tilde{P}}{\tilde{T}} = \ln\left(\frac{\tilde{v}}{\tilde{v}-1}\right) + \frac{z}{2}\ln\left(\frac{\tilde{v}+(q/r)-1}{\tilde{v}}\right) - \frac{\theta^2}{\tilde{T}} \tag{2}$$

$$\ln a_1^{\mathrm{pure}} = \ln\phi_1 + \ln\frac{\tilde{v}_1}{\tilde{v}} + q_1\ln\left(\frac{\tilde{v}}{\tilde{v}-1}\,\frac{\tilde{v}_1-1}{\tilde{v}_1}\right) + q_1\left(\frac{2\theta_1-\theta}{\tilde{T}_1} - \frac{\theta}{\tilde{T}}\right) + \frac{zq_1}{2}\ln\Gamma_{11} \tag{3}$$

where $\tilde{T}$ and $\tilde{P}$ represent the reduced temperature and reduced pressure, respectively. The equation-of-state (2) gives the corresponding reduced volume for a single component and a binary mixture, separately. Therefore, the relationship between solvent volume fraction $\phi_1$ and its activity $a_1^{\mathrm{pure}}$ can be predicted by Eq. (3). Lee and Danner have tabulated group parameters for 37 ordinary groups [23].

The parameters of pure component can be determined by a group-contribution approach, and consequently, the parameters of binary mixtures can then be estimated from pure component parameters. To improve its accuracy, a parameter representing the change of intermolecular action in mixing is introduced and can be obtained from group-interaction parameters. Thus, all the necessary parameters are predictable from only their chemical formulae.

### 2.3. The swelling-suppression effect in membranes

Swelling-suppression behavior of the filling-type membrane is described using the below equations [24]. The substrate matrix of the filling-type membrane is made of semicrystalline polymer, and the filling polymer swelling can be effectively constrained by tie-segments between crystals of the substrate matrix. The filling polymer itself is a linear polymer, which barely shows separation selectivity.

$$\ln a_1^{\mathrm{ss}} = \frac{\dfrac{V_1}{V_{\mathrm{sub}}}\left[\dfrac{\Delta H_{\mathrm{sub}}}{\mathrm{R}}\left(\dfrac{1}{T} - \dfrac{1}{T_{\mathrm{m}}}\right) + \ln a_2^{\mathrm{C}} + \ln a_2^{\mathrm{R}} + \ln a_2^{\mathrm{FV}}\right]}{\{3(v_2^{-1} + A - 1)/2f - A\}} \tag{4.1}$$

$$A = \frac{(n_{\mathrm{m}}V_{\mathrm{m}} - V_{\mathrm{p}})}{n_{\mathrm{m}}V_{\mathrm{m}}} \tag{4.2}$$

where $V_{\mathrm{m}}$ and $V_{\mathrm{p}}$ are the molar volume of the methylene unit of the polymer and the pore volume of the porous substrate, respectively. A parameter $f$ is used to express the tie-segment density of the porous substrate. Each substrate has a specific value. The porous high-density polyethylene (HDPE) film used in this work has a value of 0.15, and each filling-type membrane with the substrate should have the same value.

Consequently, the activity of a solvent in membrane $a_1^{\mathrm{m}}$ can be calculated by the addition of two terms: solvent activity in the filling polymer $a_1^{\mathrm{pure}}$ and the contribution of the swelling-suppression effect $a_1^{\mathrm{ss}}$ by the substrate. Thus

$$\ln a_1^{\mathrm{m}} = \ln a_1^{\mathrm{pure}} + \ln a_1^{\mathrm{ss}}. \tag{5}$$

### 2.4. Diffusivity

Free volume theory has been extensively studied and developed to predict diffusion in solvent–polymer systems [25–28]. Our previous study has shown its reliability to predict the diffusion coefficient in a polyacrylate filling membrane during its rubbery state [11]. The original free volume theory was derived based on amorphous rubber polymer conceptual framework [25], and a modified version extended this theory to glassy polymer regime [29]. Furthermore, we recently improved prediction accuracy of diffusion coefficient for a glassy polymer, by re-examining calculation method of effective hole free volume [16]. According to this theory, the solvent self-diffusion coefficient can be expressed by the following:

$$D_1 = D_0 \exp\left(-\frac{E}{RT}\right) \exp\left(-\frac{\gamma(w_1 V_1^* + w_2 \xi V_2^*)}{V_{FH}}\right) \quad (6)$$

where $w_i$ is the mass fraction of component $i$, and $V_i^*$ represents the specific hole free volume of component $i$ required for a diffusion jump. The average hole free volume, $V_{FH}$, per gram of mixture can be estimated by the addition of the free volumes of solvent and polymer, given by

$$V_{FH} = w_1 K_{11}[K_{21} + T - T_{g1}] + w_2 V_{FH2}. \quad (7)$$

When the system is in a rubbery state, $T > T_{g2}$, free volume theory [25] gives the following:

$$V_{FH2} = K_{12}[K_{22} + T - T_{g2}] \quad (8)$$

Considering the depression of a glass transition temperature induced by a penetrant, polymer systems maintain the equilibrium morphology of the rubbery state above the glass transition temperature $T_{gm}$ of the mixture. Consequently, Eq. (8) will be valid when operation temperature is higher than the glassy transition temperature $T_{gm}$ for a polymer mixture.

Generally, the mobility of the polymer chain greatly decreases below the glass transition temperature, $T_{gm}$, being even slower than the motion of a small molecule diffusion jump. Polymer chains only vibrate within a limited range in the form of local segmental motion, the amount of hole-free volume is almost independent of temperature, and it is regarded as a "frozen" state. The hole-free volume for a glassy polymer, effective for solvent diffusion, can be reasonably assumed as a constant equal to the corresponding value in the glass transition point. We have previously proposed a modified version of free volume theory [16], and demonstrated its validity during a limited regime near below glassy transition. A hole-free volume in this version is calculated in response to a polymer solution property, while the system enters a glassy state for $T < T_{gm}$.

$$V_{FH2} = K_{12}[K_{22} + \beta(T - T_{g2})] \quad (9)$$

The plasticization factor $\beta$ is defined as

$$\beta = \frac{T_{gm} - T_{g2}}{T - T_{g2}} \quad (10)$$

The mutual-diffusion coefficient for the solvent–polymer system is given by

$$D = D_1(1 - v_1)^2(1 - 2\chi v_1) \quad (11)$$

In this model, the available free volume parameters used for equilibrium polymer solutions, $D_0$, $E$, $V_1^*$, $V_2^*$, $K_{11}/\gamma$, $K_{12}/\gamma$, $K_{21} - T_{g1}$, $K_{22}$, $T_{g2}$, have been tabulated for common polymer and solvent systems, the value $\xi$ can be estimated by an empirical relationship [18]. The plasticization factor $\beta$, which is the only introduced parameter, can be estimated from Eq. (1). With the help of interaction parameter $\chi$ for solvent and polymer, which can be estimated by the GCLF-EOS model, a solvent mutual-diffusion coefficient can be predicted from a self-diffusion coefficient. Diffusion model includes no contribution from mobility through Langmuir sites, because solvents effectively plasticize polymers in these studied systems, and diffusion through non-equilibrium portion can be reasonably ignored. In this way, a solvent diffusion coefficient in glassy polymer systems can be estimated with Eqs. (6)–(11).

Single component flux can be calculated by integrating Fick's formula across a membrane.

$$P_1 = J_1 l = \int_{v_{m1}^P}^{v_{m1}^F} \frac{D\rho_1}{(1 - v_1)}\, dv_1 \quad (12)$$

Assuming that thermodynamic equilibrium is reached at the feed and permeate interfaces during steady state vapor permeation, Eq. (5) can be used to obtain reasonable solvent concentration in a membrane at the feed side $v_{m1}^F$. We treat the solvent concentration in the permeation side $v_{m1}^P$ as zero, because the sweep gas can dilute the permeate.

Although the behavior of a small penetrant through glassy polymer is, in general, considered to be time-dependent, and non-Fickian diffusion regime [30], no aging phenomena were observed in this preliminary study. As a matter of fact, the continuous fluctuation in a polymer matrix induced by penetrant diffusion forms a steady configuration in polymer mixtures on the whole, and consequently, allows permeability behavior to occur almost without any change over experimental time scales. Design methodology enables the prediction of solvent flux depending only on basic physical properties, without any fitting parameters from sorption, diffusion and permeation experiments. Therefore, this model is suitable for designing a filling-type membrane for a specific objective, even including the membranes whose filling polymers are not available at present.

## 3. Experimental

### 3.1. Materials

Porous HDPE film was supplied from Tonen Chemical Co. Ltd. The substrate had a thickness of 5 μm, pore size of 0.02 μm and porosity of 0.60. The grafting process has been described in detail elsewhere [12]. Using a plasma polymerization technique, a filling-type membrane, grafted by methyl methacrylate, was synthesized and will be denoted as HDPE-*g*-PMMA. Benzene and toluene were used without further purification.

### 3.2. Vapor permeation

Vapor permeation experiments of single organic vapor through HDPE-*g*-PMMA membrane were carried out. A gas sweep method was used in measuring organic vapor permeation at 25°C. The compositions of organic in feed and permeate were measured by directly introducing the penetrant into a gas chromatograph. Benzene and toluene were used as the feed.

### 3.3. Diffusion measurement

A mutual-diffusion coefficient was determined by measuring the solvent flux at 25°C with vapor permeation through a filling membrane. Actually, solvent diffusivity in a polymer is closely associated with polymer swollen state; in particular, solvent concentration in the polymer. Setting the solvent concentration in the feed side approaching to that in the permeate side resulted in an almost identical swollen state on both sides, and the solvent diffusion coefficient over all of the membrane had an averaged value.

## 4. Results and discussion

### 4.1. Effect of plasticization in glassy polymer

The introduction of organic molecules into glassy polymer gives rise to a depression of the glass transition temperature, which influences solvent solubility, diffusivity and permeability. This behavior is usually attributed to plasticization, which changes the polymer configuration by increasing the free volume of mixtures. Recently, an analysis technique developed for the measurement of positron annihilation lifetime has provided a strong tool for investigating polymer morphology [31–33], and has shown that plasticization results in a wider pore size distribution. In particular, the effect of solvent plasticization results in a change of polymer configuration, and the mobility of molecular chains tends to average, as in a rubbery state. Using Eq. (1), the depression of the glass transition temperature was calculated for benzene in PMMA as shown in Fig. 1. The glass transition temperature decreases with increasing solvent concentration. Moreover, the benzene mass fraction for isothermal glass transition at 25°C has been calculated and plotted in the figure. Benzene mass fraction of 0.19 is needed for the former to attain a rubbery state under the same temperature.

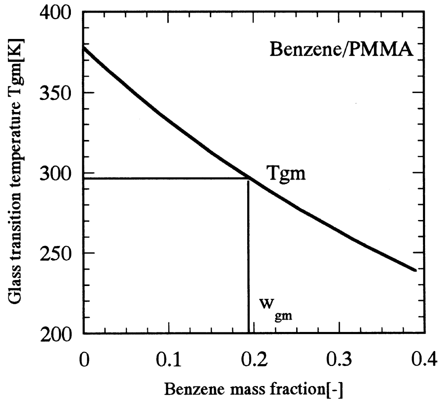

Fig. 1. Prediction of the depression of glass transition temperature with diluent mass fraction for benzene in PMMA.

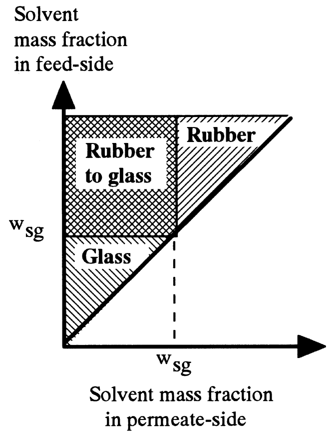

Fig. 2. Classification of the polymer state in a membrane according to the effect of plasticization, with respect to solvent concentration in feed and permeate.

For a given temperature, the solvent mass fraction corresponding to an isothermal glass transition can be estimated by Eq. (1). As can be seen in Fig. 2, the state of a polymer in a filling-type membrane is divided into different regions according to the solvent mass fraction in a filling polymer, which can be estimated using Eq. (5). For penetrant through membranes, the solvent concentration in the feed is always higher than that in the permeate. The operating point drops in the region above the diagonal line, which consists of a solvent composition for an isothermal glass transition at various operating temperatures. A polymer in a membrane may take on various states: rubbery, glassy and rubbery to glassy, in which a filling polymer changes from rubbery on the feed side towards glassy on the permeate side. The physical properties of a solvent, e.g. solubility and diffusivity, also change in different regions due to the close association between solvent behavior and polymer configuration.

Fig. 3(a) shows the sorption of benzene in PMMA, and the results of toluene sorption in the polymer are plotted in Fig. 3(b). Solvent solubility increases with its activity. Calculations from the GCLF-EOS model are in good agreement with experimental results, even below the isothermal glass transition point of these mixtures.

As shown in Fig. 3(a), when the benzene mass fraction in PMMA is less than 0.195, the polymer is in a glassy state even when the depression of glass transition is taken into account. The isothermal sorption curve, however, is different to that of normal gas sorption in glass polymers [34], in which non-equilibrium term takes a great deal of portion. Sorption of benzene in PMMA is similar to the behavior in a rubber polymer. The behavior can be found in toluene sorption in PMMA (Fig. 3(b)). Due to the plasticization effect of organic solvent, the glass transition temperature of a polymer decreases, which implies there is a change in polymer solution microstructure and intermolecular interaction.

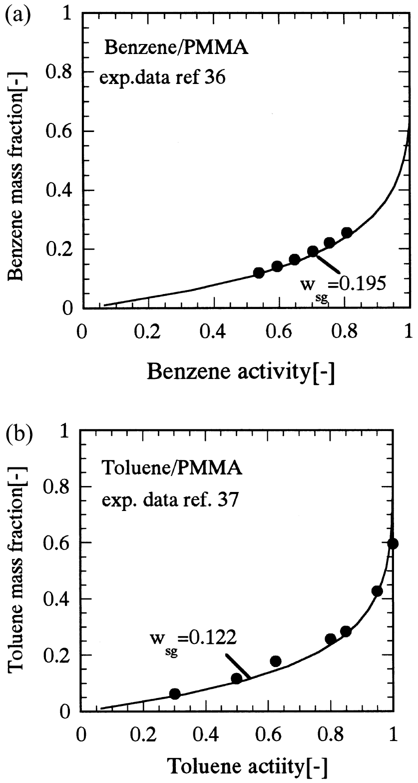

Fig. 3. (a) Solubility of benzene in glass polymer PMMA; comparison of measurement with those predicted by the GCLF-EOS model at 23.5°C. (b) Solubility of toluene in glass polymer PMMA; comparison of measurement with those predicted by the GCLF-EOS model at 48.5°C.

Emphatically, all experimental data in this study are near below the glass transition, and the rubber polymer microstructure maintains in this regime, meaning that equilibrium sorption almost dominates the behavior of vapor–liquid equilibrium. The non-equilibrium contribution from sorption in macro sites is so small that it can be ignored. In addition, sorption isotherms for benzene and polystyrene systems [35] showed similar results to this observation, and the relationship of the shape of a isotherm for glassy polymer mixture and solvent plasticization influence was investigated. Plasticization effect is obvious in these mixtures; therefore, sorption amount on non-equilibrium portion is small. The GCLF-EOS model provides satisfactory results for the whole concentration range in these studied systems.

### *4.2. Prediction of diffusivity*

While small penetrant permeates through rubbery polymer systems, free volume theory can be used to describe solvent mobility behavior. From extensive investigations of the relationship between viscosity and free volume, a mathematical model has been developed to predict the dependence of the diffusion coefficient on solvent composition and temperature in rubber polymer solutions. A lower temperature results in a decrease in polymer chain mobility, whereas the effect of plasticization accelerates polymer chain motion. The rubbery state in a polymer mixture can even extend below the glass transition temperature of a pure polymer. Therefore, we can reasonably assume that the mobility of both a small molecular penetrant and a polymer chain remains the same until the glass transition temperature of the polymer mixture $T_{gm}$ is reached. The same diffusion model is used for this range.

Using free volume theory, diffusion of a low molecular weight solvent in polymer is determined by the quantity of hole free volume, effective for diffusion jumps. A lack of active energy in a glassy polymer system retards polymer chain mobility. Consequently, the vibration of a polymer chain is limited to the region around its balance position as a local motion. The hole-free volume for a polymer can be considered to be approximately constant and equal to that value corresponding to a glass transition.

Fig. 4 shows a compositional dependence of the solvent diffusion coefficient for benzene in PMMA. The solubility model shown in Eq. (5) determines solvent concentration in filling polymers. The value of solvent composition for an isothermal glass transition is estimated by Eq. (1) at 25°C. As shown in Fig. 4, the mutual-diffusion coefficient exponentially decreases with the decease of benzene concentration in PMMA, while benzene volume fraction is higher than the value (0.243) for an isothermal glass transition. Obviously, the same transition point is effective for diffusion; the compositional dependence of diffusion coefficient tends to relax below this point. Prediction results from a diffusion model were in good agreement with experimental results during the studied solvent concentration range, while prediction of the original free volume theory obviously deviates from experiment. Since PMMA has a relatively high glass temperature, the concentration required for an isothermal glass transition is also high. No experimental data were obtained above the concentration of 0.243 for an isothermal glass transition, and consequently, a

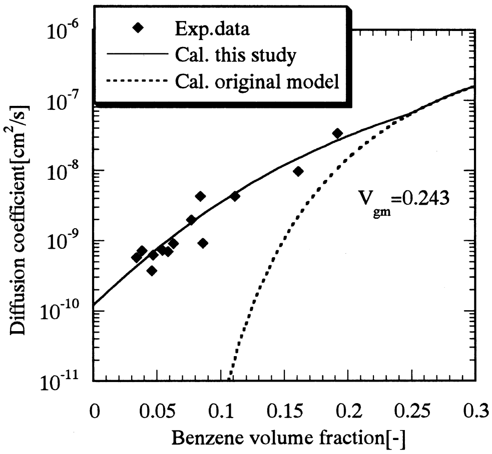

Fig. 4. Dependence of the mutual-diffusion coefficient of benzene on its concentration in PMMA at 25°C, and a comparison with that calculated from free volume theory.

comparison of the predicted with the measured results is limited to the glassy regime.

### *4.3. Prediction of vapor permeation*

Generally, permeability of small penetrants through membranes is dominated by not only solubility but also diffusivity. Due to the presence of an isothermal transition point for the diffusion coefficient in a glassy polymer mixture, the dependence of solvent flux on activity in feed varies above and below this point. As can be seen in Fig. 5(a), the prediction of benzene flux through HDPE-*g*-PMMA membrane shows that the flux increases almost exponentially with solvent activity in feed. Its slope has a turn around isothermal glass transition activity of 0.90. Below this value, the filling polymer in a membrane remains completely in a glassy state, because solvent activity in the feed remains always higher than that in permeate. For the same reason, as solvent activity in feed is above this value, the filling polymer near the feed is a rubbery state, while the part near the permeate side remains a glassy polymer. All experimental data were measured within glassy PMMA membrane, and benzene flux in vapor permeation is approximately consistent with the prediction. An investigation of toluene (Fig. 5(b)) has shown similar results, with the exception of a lower permeation rate than benzene. Owing to the slow local mobility of polymer segment in glassy PMMA, vapor permeation takes a much long time to attain a steady state and experimental results scatter in a wide range.

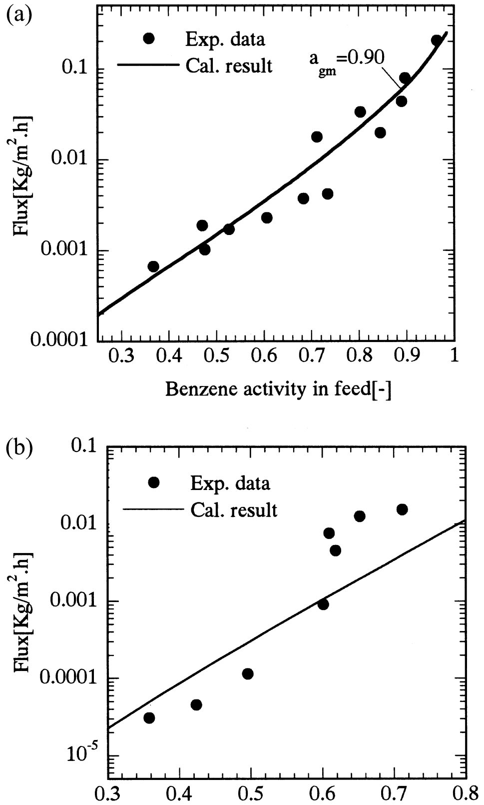

Fig. 5. (a) Benzene flux through HDPE-*g*-PMMA membrane across the glass transition point during vapor permeation at 25°C and a comparison with calculations. (b) Toluene flux through HDPE-*g*-PMMA membrane across the glass transition point in vapor permeation at 25°C and a comparison with calculations.

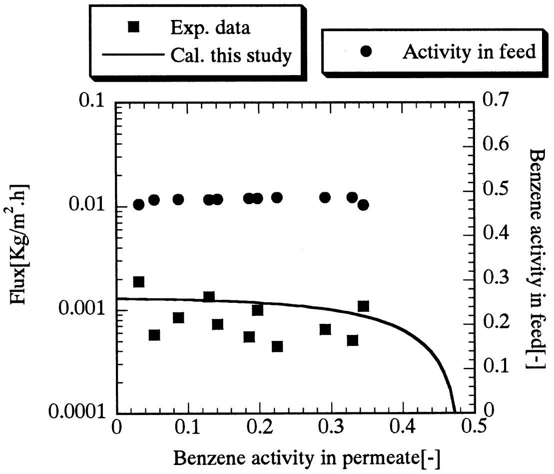

Fig. 6. Dependence of benzene flux on its activity in permeate side of HDPE-*g*-PMMA membrane at 25°C and a comparison with this calculation.

The dependence of flux on solvent activity in permeate has also been investigated with a constant benzene activity in the feed of around 0.48. As can been seen in Fig. 6, calculated benzene flux through a HDPE-*g*-PMMA membrane rapidly increases with the decrease in the activity in permeate, and then relaxes towards a constant value. Calculation results are approximately in agreement with measurements. Based on these results, solvent activity in permeate does has little influence on its flux for certain ranges, unless it is higher than a critical value. This conclusion might be helpful for determining appropriate operating conditions.

## 5. Conclusions

The design method for a filling-type membrane was extended to a glassy polymer membrane, by investigating solvent solubility and diffusivity in glassy PMMA. Prediction of solubility, diffusivity and swelling suppression of substrate enabled the prediction of solvent flux, which shows different trends corresponding to various ranges; above or below solvent concentration for an isothermal glass transition. A peculiarity of the present approach is that solvent permeability can be calculated solely from the estimation of polymer physical properties, without using fitting parameters from sorption, diffusion or permeation experiments, thus giving a completely predictive method. These predictions are in good agreement with experimental data.

Taking into account the plasticization induced isothermal glass transition, the modified free volume model was employed to estimate solvent diffusivity in a glassy polymer. A solvent diffusion coefficient calculated using this approach is in good agreement with experimental results.

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