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Sorption/desorption properties of water vapour in poly(2-hydroxyethyl methacrylate): 2. Two-stage sorption models

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The two-stage integral sorption data for water vapour in a glassy poly(2-hydroxyethyl methacrylate) (PHEMA) membrane are analysed by the variable-surface concentration model, the diffusion–relaxation model, and the diffusion–reaction model. Satisfactory fitting of the data and similar kinetic and equilibrium parameters are obtained using these models. The diffusion coefficient for water is about 5.0×10^{-7} cm^2 s^{-1} in the glassy polymer at 37°C and is near 1.5–2 times higher as the polymer goes over the glass–rubber transition region due to water sorption. The relaxation rate constant is between 1.0 and 5.1×10^5 s^{-1} and is increased as the sorbed concentration or the vapour activity of water increases. The equilibrium ratio constant is between 0.15 and 0.21 for the cases in which the polymer is characterized to be in the glassy state, and between 0.06 and 0.1 for the case in which the polymer passes the glass–rubber transition. When the two-stage sorption prevails, the diffusion–relaxation model approximates the limiting cases of the other two models. The diffusion–reaction model, based on Fickian diffusion and a reversible first order reaction kinetics for the penetrant transfer between the immobilized and mobile modes, is superior to the other two in terms of completeness of description of physical phenomena. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

It is well known that non-Fickian sorption is a common behaviour for a polymer-penetrant system below its glass transition temperature[1–3]. The slow relaxation of the polymer chains due to sorption of penetrant is used to interpret the anomalies in the sorption kinetics. When a penetrant enters the polymer matrix, motions of whole or portions of glassy polymer chains are not sufficiently rapid to completely homogenize the penetrant's environment. Penetrants can thus potentially rest in holes or irregular cavities with very different intrinsic diffusional mobilities[3].

The relative magnitude of the rates of diffusion and relaxation processes is a major factor determining the anomalous effects in polymer–penetrant diffusion. A diffusion Deborah number was proposed by Vrentas *et al.*[4] to characterize the quantity. This dimensionless number is defined as

$$(DEB)_{\mathrm{D}} = \frac{\lambda_{\mathrm{m}}}{\theta_{\mathrm{D}}} \tag{1}$$

where λ_{m} is the characteristic time of the relaxation and θ_{D} the characteristic diffusion time given by L_{o}^2/D, with L_{o} the sample dimension in the direction of transport and D the diffusion coefficient. A general definition of the characteristic time λ_{m} was given by Vrentas and coworkers[4–6], but a simplified one will be considered here. If the relaxation follows a first-order kinetics[7–10], the characteristic time λ_{m} is represented by the reciprocal of the first-order rate constant k. The diffusion Deborah number can be expressed as

$$(DEB)_{\mathrm{D}} = \frac{D}{kL_{\mathrm{o}}^2} \tag{2}$$

Which is actually the ratio of the diffusion rate of a penetrant to the relaxation rate of the polymer system with a dimension L_{o}. When both the rates of diffusion and relaxation are similar in magnitude, anomalous diffusion takes place in the polymer matrix. On the other hand, when one of them is much larger than the other, Fickian diffusion will dominate. For $(DEB)_{\mathrm{D}} \gg 1$, the diffusion is much faster than the response of the polymer relaxation and the glassy state is preserved, the 'elastic' Fickian diffusion prevails. While for $(DEB)_{\mathrm{D}} \ll 1$, the polymer relaxes to a rubbery state in a speed much faster than the diffusion of the penetrant, the 'viscous' Fickian diffusion is expected. If $(DEB)_{\mathrm{D}}$ is of the order of unity, the diffusion process can be described as 'viscoelastic'[11,12].

Two-stage sorption is one of the notable non-Fickian features of glassy polymer system, and it has been observed by many authors[7–15]. In Part I of this series, we also observed the two-stage sorption from an integral sorption experiment of water vapour in a glassy PHEMA membrane[16]. An effort was attempted to correlate the data with available mathematical models to track down the kinetic and equilibrium parameters of the system. The variable surface-concentration model proposed by Long and Richman[7] gave a satisfactory fitting of the experimental data[17]. In a continuation of this effort, it has been found that the diffusion–relaxation model proposed by Berens and Hophenberg[8] and the diffusion–reaction model[10,18] also gave similar results.

In this paper, mathematical analysis of our experimental data by these models is reported. A unified approach in formulating these models is presented, and the transport of the system can be characterized by several dimensionless numbers as defined in this approach. By comparing some similar and different features of these three models, a general discussion of the advantages and limitations of these models is presented.

THEORETICAL MODELS

Variable surface-concentration model (Model I)

This model was proposed by Long and Richman[7], and was probably the first one to provide a reasonable explanation for two-stage sorption behaviour.

According to the Fick's second law, the diffusion equation within the membrane is given as:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \tag{3}$$

The experimental condition gives the initial condition

$$t < 0 \qquad C = 0 \qquad 0 \leq x \leq L \tag{4}$$

where L is the half-thickness of the membrane. The model of variable surface concentration assumes that the concentration at the membrane surface ($x = L$) jumps to C_0 as soon as the membrane contacts the vapour and then reaches a final concentration C_∞ following a first order relaxation process[7]. Symmetry of the concentration at the centre ($x = 0$) of the membrane is assumed.

The boundary conditions are:

$$t \geq 0 \begin{cases} C = C_0 + (C_\infty - C_0)(1 - e^{-kt}) & x = L \\ \dfrac{\partial C}{\partial x} = 0 & x = 0 \end{cases} \tag{5}$$

where k is the rate constant of the relaxation process. The governing equation (3) is solved by assuming constant diffusivity D_0 and using the following dimensionless variables:

$$z = \frac{x}{L} \qquad \bar{C} = \frac{C}{C_\infty} \qquad \theta = \frac{D_0 t}{L^2} \qquad \psi = \frac{kL^2}{D_0} \qquad \phi = \frac{C_0}{C_\infty} \tag{6}$$

where θ is the dimensionless time, ψ is the inverse of the diffusion Deborah number $(DEB)_\mathrm{D}$, and ϕ is the equilibrium ratio constant which represents the ratio of the equilibriums of the first stage to that of the second stage in the sorption. The solution of the dimensionless concentration is:

$$\bar{C}(z,\theta) = \phi\left[1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)}\cos\left(\frac{(2n+1)\pi z}{2}\right)\exp\left(-\frac{(2n+1)^2\pi^2\theta}{4}\right)\right]$$

$$+ (1-\phi)\left(1 - \frac{\cos(\sqrt{\psi}z)\exp(-\psi\theta)}{\cos\sqrt{\psi}} - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)\left(1 - \dfrac{(2n+1)^2\pi^2}{4\psi}\right)}\cos\left(\frac{(2n+1)\pi z}{2}\right)\exp\left(-\frac{(2n+1)^2\pi^2\theta}{4}\right)\right) \tag{7}$$

Integration of the dimensionless concentration over $z = 0$ to $z = 1$ yields the fractional weight uptake as function of dimensionless time θ.

$$\frac{M_t}{M_\infty} = \phi\left(1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{\exp\left(\dfrac{-(2n+1)^2\pi^2\theta}{4}\right)}{(2n+1)^2}\right)$$

$$+ (1-\phi)\left(1 - \frac{\tan\sqrt{\psi}\exp(-\psi\theta)}{\sqrt{\psi}} - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{\exp\left(\dfrac{-(2n+1)^2\pi\theta}{4}\right)}{(2n+1)^2\left(1 - \dfrac{(2n+1)^2\pi^2}{4\psi}\right)}\right) \tag{8}$$

Equation (8) is intrinsically the same as the expression proposed by Long and Richman[7] except that different notations are used here. The first part on the right-hand side of equation (8) represents the classical Fickian diffusion to the quasi-equilibrium (first stage), and is the weight uptake for the penetrant which enters due to diffusion down the concentration gradient set up by the initial surface concentration. The second part is for the penetrant which enters as a result of the time dependence of the surface concentration change.

Diffusion–relaxation model (Model II)

Berens and Hopfenberg[8] proposed this model by considering the sorption process in glassy polymers as a linear superposition of phenomenologically independent contributions from Fickian diffusion and polymeric relaxation. The initial diffusion-controlled sorption is more rapid than the long term relaxation in their experiments with submicron particles, permitting explicit separation of the entire sorption process into two seemingly independent mechanisms. The fractional uptake with the dimensionless time θ is expressed as

$$\frac{M_t}{M_\infty} = \phi\left(1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{\exp\left(\frac{-(2n+1)^2\pi^2\theta}{4}\right)}{(2n+1)^2}\right) + (1-\phi)[1-\exp(-\psi\theta)] \tag{9}$$

for a slab geometry, such as a membrane, if a single first order relaxation process is considered. Where ϕ is the same as that described in Model I but also can be interpreted as the fraction of the equilibrium amount of sorption in the unrelaxed polymer to that in the fully relaxed polymer, and θ and ψ carry the same meaning as those in Model I. In a later comment, Joshi and Astarita[9] suggested that equation (9) cannot be right unless the characteristic diffusion time is much smaller than the characteristic relaxation time, that is, $\psi \ll 1$. This context will be discussed later in the part on *limiting behaviours* of this section and the part on *sorption curves of the three models* in the Results and Discussion section.

In the original model presented by Berens and Hopfenberg[8], there may be more than one relaxation process with different relaxation times distributed in the polymer matrix. The second part on the right-hand-side of equation (9) will be expressed as a summation of these parallel first order processes with various relaxation rate constants. However, only a single relaxation process is considered here for simplicity.

Diffusion–reaction model (Model III)

The concept of this model is not a new one. Many publications have proposed the basic assumptions and discussed some of the mathematical treatments[10,18–21], but it was not until the work by Kang *et al.*[10] that a clear mathematical solution for a spherical system was explicitly presented. Physically, the model is conceived as the so-called 'dual-mode' sorption model, in which the penetrant is distributed in two types of sorption modes, one allows penetrant to diffuse freely, and the other immobilizes the sorbed penetrant limiting its movement. The key assumption is that the transfer between two modes is equivalent to a first-order reversible reaction.

$$C_A \underset{k}{\overset{k'}{\rightleftharpoons}} C_B \tag{10}$$

where C_A and C_B are the concentrations of the diffusing (A) and the immobilized (B) species, and k' and k represent the rate constants of the forward and the backward reactions, respectively. The notation of the backward constant is the same as that of the relaxation rate constant used in the previous two models because the inverse of an immobilization reaction is also a kind of relaxation process of the bonding between the immobilized molecules and the fixing sites. The sites where the penetrant is immobilized can be either holes or irregular cavities within the glassy polymer structure[3] but also can be special functional groups which interact with the penetrant as we postulated in Part I[16]. The equilibrium constant for these reactions is defined as $K(=k'/k)$, and it can be thought to be a distribution coefficient of the penetrant in the two sorption modes. The differential mass balances for A and B within the membrane give the following differential equations:

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C_A}{\partial x}\right) - k(KC_A - C_B) \tag{11}$$

$$\frac{\partial C_B}{\partial t} = k(KC_A - C_B) \tag{12}$$

The initial and boundary conditions are:

$$t < 0 \quad C_A = C_B = 0 \quad 0 \le x \le L$$

$$t \ge 0 \begin{cases} C_A = C_A^S = C_0 & x = L \\ \dfrac{\partial C_A}{\partial x} = 0 & x = 0 \end{cases} \tag{13}$$

where C_A^S is defined by equilibrium of species A with outside vapour phase at the surface ($x = L$) and is equivalent to the C_0 used in equation (5) because the equilibrium is achieved as soon as the membrane is in contact with the vapour phase. Solution for equation (12) at the surface will lead to the following relationship

$$C^S = C_A^S + C_B^S = C_0[1 + K(1 - e^{-kt})] \tag{14}$$

where C^S and C_B^S are the concentrations of the total (A and B) and the immobilized (B) species. The final total concentration at the surface (C_∞^S) as well as that within the membrane (C_∞) can be obtained from equation (14) as $t \to \infty$.

$$C_\infty = C_\infty^S = C_0(1 + K) \tag{15}$$

The fractional contribution of the free diffusing species to the final uptake, ϕ, is related to K by

$$\phi = \frac{C_0}{C_\infty} = \frac{1}{1+K} \tag{16}$$

It has been recognized that the behaviour at the surface is the same as that in the variable surface-concentration model (Model I)[10] and the first boundary condition in equation (5) can be readily derived from equations (14) and (15).

The governing equations (11) and (12) are solved similar to the procedures in Model I by assuming constant diffusivity D_0 and using the same dimensionless variables defined in equation (6). The method of Laplace transform is used to obtain the solutions[10,18].

The dimensionless concentrations of the free diffusing species ($\overline{C_A}$) and immobilized species ($\overline{C_B}$) are given, respectively, as

$$\bar{C}_A(z,\theta) = \phi\left[1 + \sum_{n=0}^{\infty}\frac{(-1)^n(2n+1)\pi\cos\frac{(2n+1)\pi}{2}z}{s_n\left(\frac{d\Phi}{ds}\right)_{s_n}}e^{s_n\theta}\right] \tag{17}$$

$$\bar{C}_{\mathrm{B}}(z,\theta) = (1-\phi)\left[(1-\mathrm{e}^{-\psi\theta}) + \psi\sum_{n=0}^{\infty}\frac{(-1)^n(2n+1)\pi\cos\frac{(2n+1)\pi}{2}z}{s_n(s_n+\psi)\left(\frac{\mathrm{d}\Phi}{\mathrm{d}s}\right)_{s_n}}(\mathrm{e}^{s_n\theta}-\mathrm{e}^{-\psi\theta})\right] \tag{18}$$

where $(\mathrm{d}\Phi/\mathrm{d}s)_{s_n} = [s_n^2 + 2\psi s_n + \psi^2(1+K)]/(s_n+\psi)^2$, and s_n are nonzero roots of

$$s + \frac{\psi K s}{s+\psi} = -\frac{(2n+1)^2\pi^2}{4} \quad \text{as} \quad K = \frac{1-\phi}{\phi}$$

The fractional weight uptake as a function of dimensionless time θ is obtained by the integration of equations (15) and (16) over space.

$$\frac{M_{\mathrm{t}}}{M_\infty} = \phi\left[1 + \sum_{n=0}^{\infty}\frac{2\mathrm{e}^{s_n\theta}}{s_n\left(\frac{\mathrm{d}\Phi}{\mathrm{d}s}\right)_{s_n}}\right] + (1-\phi)\left[(1-\mathrm{e}^{-\psi\theta}) + \psi\sum_{n=0}^{\infty}\frac{(\mathrm{e}^{s_n\theta}-\mathrm{e}^{-\psi\theta})}{s_n(s_n+\psi)\left(\frac{\mathrm{d}\Phi}{\mathrm{d}s}\right)_{s_n}}\right] \tag{19}$$

The result is similar to that in equation (8). The first part on the right-hand side of equation (19) represents the contribution from the free diffusing species, and the second part is for that from the immobilized species.

The ψ in this model represents the square of Thiele modulus, a term often used in heterogeneous catalysis to characterize the simultaneous diffusion and reaction in the pores of catalyst particles, and can be considered as a relative magnitude of the first order reaction rate to the diffusion rate of a reactant. Note that the backward reaction rate constant is used in the definition of ψ and it is an indication of how fast the equilibrium of the reaction in equation (10) may reach. The mathematical treatment of this model takes into account the aspects of simultaneous diffusion and reaction as mentioned above, and thus the model is referred to as a 'diffusion–reaction model' in this text.

Limiting behaviours

In above models, equations (8), (9) and (19) depict the sorption behaviour which combines the Fickian diffusion and a first order relaxation process. All of them indicate that if ϕ is known the fractional uptake (M_{t}/M_∞) with dimensionless time (θ) only depends on the magnitude of ψ, that is, the reciprocal of the diffusion Deborah number ($(DEB)_{\mathrm{D}}$). Therefore, the relative magnitude of the rates of the diffusion and the relaxation processes determines the behaviour of sorption.

Although the assumptions of the models and the mathematical forms of equations (8), (9) and (19) are different, they perform similarly when ψ is much smaller than unity [$\psi \ll 1$ or $(DEB)_{\mathrm{D}} \gg 1$]. The second term on the right-hand side of equation (8) reduces to $(1-\phi)[1-\exp(-\psi\theta)]$, and equation (8) becomes equation (9). In equation (19), the eigenvalues $s_n \approx -(2n+1)^2\pi^2/4$, $(\mathrm{d}\Phi/\mathrm{d}s)_{s_n} \approx 1$, and it may require $K(=(1-\phi)/\phi)$ not too large to hold the relation of $\psi K \ll \pi^2/4$, and accordingly, equation (9) can be derived for this case. This situation confirms that the diffusion–relaxation model can be a good approximation to the sorption behaviour when $\psi \ll 1$[8,9].

On the other hand, equations (8), (9) and (19) perform very differently when ψ is much larger than unity ($\psi \gg 1$ or $(DEB)_{\mathrm{D}} \ll 1$). Equation (8) reduces to the standard Fickian diffusion form as

$$\frac{M_{\mathrm{t}}}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{\exp\left(\frac{-(2n+1)^2\pi^2\theta}{4}\right)}{(2n+1)^2} \tag{20}$$

It means that the surface concentration jumps to the final equilibrium in a very fast rate. The boundary condition at $x = L$ of equation (5) becomes $C = C_\infty$, as in the case for standard Fickian sorption. As $\psi \gg 1$, equation (9) gives

$$\frac{M_{\mathrm{t}}}{M_\infty} = \phi\left(1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{\exp\left(\frac{-(2n+1)^2\pi^2\theta}{4}\right)}{(2n+1)^2}\right) + (1-\phi) \tag{21}$$

where the fractional uptake jumps to a fraction of $1-\phi$ in the beginning of the sorption, then follows the Fickian behaviour for the rest of the journey. Physically, this cannot be true in reality and it is probably a drawback of the diffusion–relaxation model. The eigenvalue is $s_n \approx -(2n+1)^2\pi^2/4\ (1+K) = -(2n+1)^2\pi^2\phi/4$ and $(\mathrm{d}\Phi/\mathrm{d}s)_{s_n} \approx 1 + K = 1/\phi$ in equation (19) as $\psi \gg 1$, and it leads to

$$\frac{M_{\mathrm{t}}}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{\exp\left(\frac{-(2n+1)^2\pi^2\phi\theta}{4}\right)}{(2n+1)^2} \tag{22}$$

where ϕ is the equilibrium ratio constant which represents the fraction of the free diffusing species to the final uptake. If the dual-mode sorption model is applicable, this equation describes the situation that the equilibrium between the two modes establishes instantaneously as soon as the diffusing species reaching the position of consideration within the membrane. The sorption follows Fickian-like behaviour, but it resembles a result which is with a diffusion coefficient of ϕD_{o}. For ϕ equal to 1, equation (22) will be identical to equation (20).

EXPERIMENTAL AND NUMERICAL ANALYSIS

The experimental method and procedures were essentially the same as those described in Part I[16]. The integral sorption data of water vapour in glassy PHEMA membrane at 37°C were taken for analysis in this article. The parameters D_0, ϕ and ψ were identified for

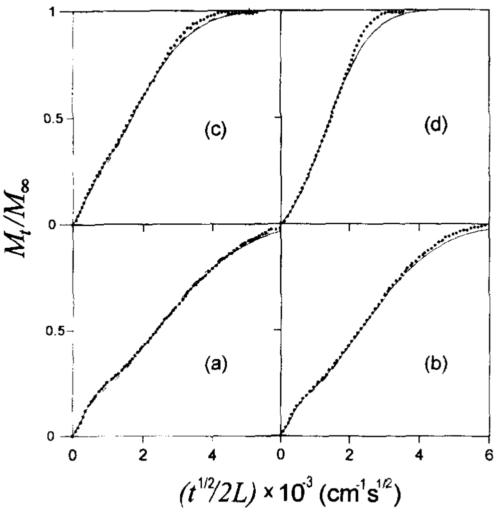

Figure 1 Sorption kinetics of water into a PHEMA membrane at 37°C, where the water vapour activity and the equilibrium water content are 0.20 and 0.017 for (a), 0.37 and 0.036 for (b), 0.51 and 0.044 for (c), and 0.72 and 0.093 for (d), respectively. The symbol (●) represents experimental data, and the lines (————, — — — — — — — and — — — —) represent the simulated results by Models I, II, and III, respectively

the sorption data by a nonlinear regression routine from the IMSL library: DUNLSF, which based on a modified Levenberg–Marquardt algorithm along with a finite-difference Jacobian[22].

RESULTS AND DISCUSSION

Fitting of experimental data

The three models derived above were tested with four data sets from previous study on water vapour sorption in PHEMA membrane (*Figure 1*). The simulations demonstrate that all three models are capable of describing the main features of the sorption process. The characteristic knee of the two-stage sorption is perfectly reproduced in *Figures 1a–c*, and the slightly sigmoidal behaviour of *Figure 1d* is also shown. However, the difference among the three models is hardly distinguishable because of overlapping of curves.

The parameters D_0, ϕ and ψ for these data sets were determined as described previously (*Table 1*). The value of the relaxation/reaction rate constant k is also given according to the equation (6) with $L = 0.023$ cm. For the same data set, the values of these parameters obtained from the three models are close enough, because these models are similarly based on the same assumptions of Fickian diffusion with a constant diffusion coefficient and first-order relaxation[10].

According to the values of these parameters and the shapes of these curves, the data sets can be classified as two types. The **a**, **b** and **c** sets (refer to the data shown in *Figures 1a–c*, respectively) belong to one type, and the **d** set (refer to the data shown in *Figure 1d*) is another type. From previous study, we knew that the sorption equilibrium of the system is below the $C_g(T)$, which is the water content when the polymer has a glass–rubber transition at temperature T, for the former type[23], and above the $C_g(T)$ for the latter type. Therefore the sorption of the former type is in the glassy state, and that of the latter type passes through the glass–rubber transition point.

All of the three models give nearly a constant diffusion coefficient *ca* 5.0×10^{-7} cm^2 s^{-1} for water in the glassy PHEMA membrane. A higher diffusion coefficient value is obtained from each model for the **d** set as the vapour activity is high enough to induce the glass–rubber transition in this case. The results may also imply that a diffusion coefficient of small penetrant is independent of its concentration in a glassy polymer as the free volume available for diffusion is not changed by sorption, but increases with its concentration in a rubbery polymer due to the increased free volume by the swelling effect of the penetrant. It should be noted that the experiment was operated in an integral manner, the diffusion coefficient as well as the rate constant of relaxation/reaction, which will be discussed later, is an average one from those for the water concentration between the initial (zero) and the final equilibrium.

The magnitude of the ratio constant ϕ is slightly different for different models and is between 0.15 and 0.21 for the glassy state type, and between 0.06 and 0.1 for the type passing through the glass–rubber transition. The interpretation of these data is not universal and is dependent on the model under consideration.

Table 1 Values of the parameters for each model to simulate the experimental results in *Figure 1*

Experimental data set	Model	D_0 $\times 10^7$ (cm^2 s^{-1})	ϕ	ψ	k $\times 10^5$ (s^{-1})
	I	4.504	0.2018	0.0477	1.015
a	II	4.621	0.1885	0.0466	1.018
	III	5.290	0.1835	0.0469	1.173
	I	5.034	0.1657	0.0494	1.175
b	II	5.202	0.1513	0.0478	1.175
	III	5.290	0.1675	0.0513	1.283
	I	4.654	0.2039	0.0965	2.122
c	II	4.924	0.1764	0.0914	2.127
	III	5.290	0.1937	0.1023	2.558
	I	7.308	0.0939	0.1032	3.564
d	II	7.624	0.0633	0.0984	3.545
	III	10.580	0.0814	0.1013	5.065

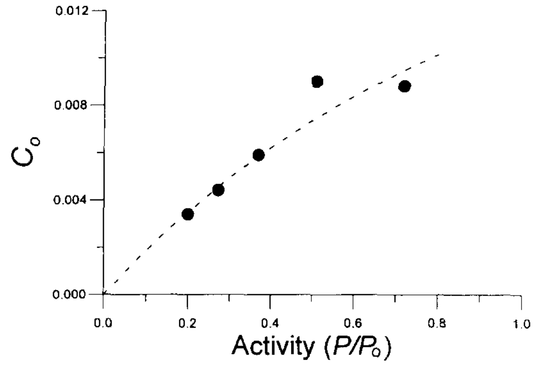

Figure 2 The initial surface concentration of water content in the PHEMA membrane as function of water vapour activity at 37°C

In the variable-surface concentration model, the ratio constant ϕ represents the ratio of the equilibria of the first stage to that of the second stage in sorption, and the initial surface water content C_0 can be determined (as shown in *Figure 2*). The relationship between C_0 and vapour activity represents a certain sorption isotherm as indicated by the dashed line. The physical significance of C_0 can be conceived as the sorption equilibrium for the glassy polymer before relaxation. However, it is only a pseudo-equilibrium of the polymer–penetrant system since the final equilibrium shifts when penetrant enters the polymer matrix.

In the diffusion–relaxation model, the ratio constant ϕ is the ratio of the amount of sorption at equilibrium in the unrelaxed polymer to that at final equilibrium, which carries a similar meaning as that in the variable-surface concentration model but its values are slightly lower.

According to the diffusion–reaction model, the reaction equilibrium constant (K) or the distribution coefficient of the two modes for a penetrant can be determined from the ratio constant ϕ by equation (16). The distribution coefficient between the immobilized and mobilized water molecules was found to be 4.5 (an average of the data sets **a**–**c**) in the glassy PHEMA and 11.3 for the set **d** passing through the glass–rubber transition. The results indicate that a rubbery polymer may provide more sites for penetrant to stay, and for diffusion, the effective number of free molecules available is much lower than that of sorbed ones. In this context, the distribution coefficient may not be a constant pending on the state of polymer structure.

The dimensionless number ψ is the ratio of the characteristic diffusion time to the characteristic relaxation/reaction time in the polymer/penetrant system. With a data range from 0.046 to 0.103, it indicates that the characteristic time of the relaxation or the exchange between two different modes is about 9–22 that of the diffusion time. The number ψ and the calculated rate constant k tend to be larger as the polymer is close to or

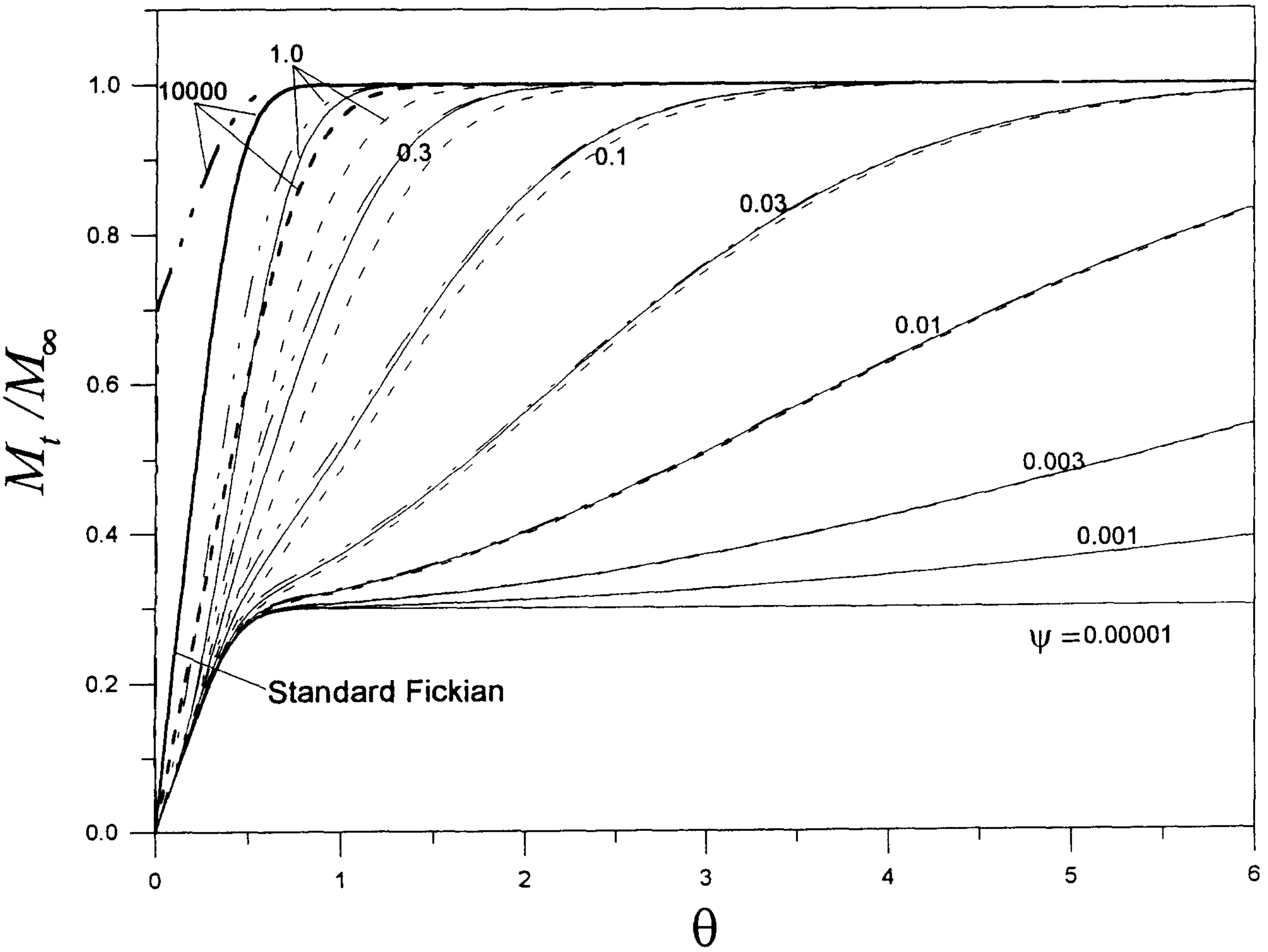

Figure 3 Parametric study for the three models: variation of the dimensionless group (ψ) to the relationship between the fractional uptake and the reduced time (θ) while ϕ is kept constant at 0.3. The lines (————, — - - — - - —, and — — — —) represent the simulated results by Models I, II, and III, respectively. The thick lines for the three models on the left part of the figure represent the results for ψ = 10000 and above

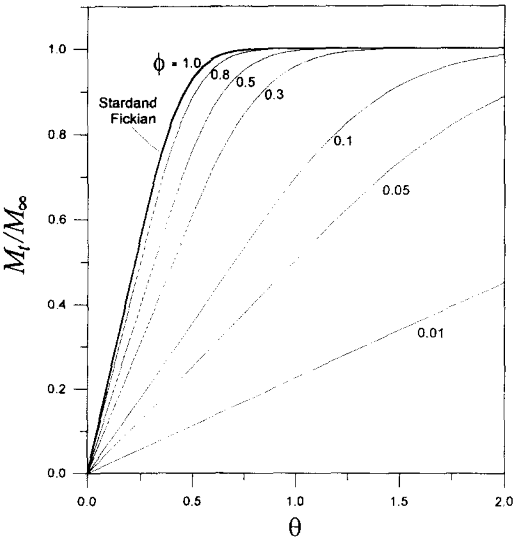

Figure 4 Limits of the diffusion–reaction model when ψ is very large: variation of the dimensionless group (ϕ) to the relationship between fractional uptake and reduced time (θ) while ψ is kept at 10000 or above

passing through the glass–rubber transition point and may be increasing functions of penetrant concentration or activity. This postulation is reasonable because the system responds rapidly as the penetrant swells the polymer to enhance the mobility of polymer chains.

In the model simulations for experimental data, deviation is found at a later stage of sorption, and becomes more obvious when the vapour activity is higher. The deviation can be minimized by modifying the models with concentration-dependent (or activity-dependent) diffusion coefficient or relaxation rate constant. However, this extension is out of the scope of this work and will not be discussed further.

Sorption curves of the three models

As long as ϕ and ψ are fixed, a sorption curve can be drawn for the theoretical fractional weight uptake with dimensionless time θ in each model. *Figure 3* shows the sorption curves with different ψ for these three models. Since ϕ only determines the height of the first stage, an arbitrary number of 0.3 is chosen without losing the generality in discussing the features of the sorption curves.

Several interesting results shown in *Figure 3* deserve attention, and reflect the *limiting behaviours* in the previous section. Primarily, all three models perform similar two-stage sorption behaviours when $\psi < 0.1$, and the sorption curves are almost the same as $\psi < 0.01$. In this case, equation (9) can be a good approximation to the curves for three models. When ψ is very small, the curves are overlapped together and a Fickian curve is observed up to the first stage, followed by a very long time to reach the second stage. When $\psi > 0.3$, the curves of the three models with the same ψ become further and further apart from each other as ψ increases. Some of the sigmoidal behaviours are observed for the curves with ψ about 0.3–1.When ψ is very large, the curve of each model approaches an asymptote, whose line thickens in the plot. From left to right, the three thick lines on the left part of *Figure 3* are the graphical representation of equations (21), (20), and (22), respectively.

General remarks on the three models

The three models are similar in describing the two-stage sorption behaviours. All of them are based on the assumption of Fickian diffusion and some kind of first order relaxation kinetics. The outcomes of these models are similar when ψ is small, but deviate when ψ is large as we discussed above. The nature of the assumptions in these models also lead to some advantages and limitations in application of these models.

The diffusion–relaxation model provides a simpler equation to describe the two-stage behaviours and can be a very good approximation to the other two models when ψ is small. However, the model fails when the diffusion and relaxation are coupled[9], or in other words the relaxation time is comparable to or smaller than the diffusion time. In the extreme case, equation (21) is not valid; therefore, the physical ground of this model is not as strong as the other two. Furthermore, the concentration profile of the penetrant within the polymer membrane is not revealed by this model, whereas equation (7) in the variable surface-concentration model, and equations (17) and (18) in the diffusion–reaction model can describe the concentration profile.

Both the variable surface-concentration model and the diffusion–reaction model have the same penetrant concentration profile with time at the surface of the membrane, which has been confirmed experimentally[24,25], but the physical conditions within the membrane are different for them. The relaxation of the polymer chains only takes place at the surface for the former model, while relaxation exists throughout the whole membrane for the latter. Thus, the variable concentration model only considers the surface relaxation, the diffusion–reaction model also considers the internal relaxation. The situation may be favourable for the diffusion–reaction model to describe the real physical phenomenon within the polymer membrane.

Depending on the ratio constant ϕ, an asymptote of the sorption curve appears as ψ is infinite for the diffusion–reaction model. *Figure 4* shows the sorption curves for various values of ϕ when ψ is equal to or larger than 10000. Each of the curves is still Fickian-like and the curve becomes standard Fickian when ϕ is one. Other than the standard Fickian curve, each of the curves looks like a Fickian sorption with a diffusion coefficient of ϕ D_0. The situation implies that the apparent or measured diffusion coefficient may be lower than the 'true' one (D_0), if a polymer consists of a large number of 'sites or holes' or functional groups, which can temporarily attract the penetrant to be attached even if the exchange rate between the immobilized molecules and mobile ones is very fast. This may be a cause of a concentration-dependent diffusion coefficient because ϕ may be a function of the penetrant concentration in the polymer. It is difficult to verify this postulation unless the mean residence time of each molecule on the 'site' can be measured prior to the sorption experiment, because simply a curve fitting or regression analysis of sorption data with the equations of the current model would lead to a biased result. Further investigation is needed to clarify this point.

CONCLUSIONS

The variable surface-concentration model, diffusion–

relaxation, and diffusion–reaction model are reformulated in a unified approach. Three dimensionless numbers 'ϕ, ψ and θ' are identified to fully characterize the fractional weight uptake in these models. Comparisons are made by testing these models with experimental data and by parametric studies to find out the advantages and the limitations of these models. All three models can satisfactorily describe the experimental data of water vapour sorption in a glassy PHEMA membrane in an integral operation manner, no matter that the polymer is still in the glassy state or has passed through the glass–rubber transition point at final equilibrium. The plots of the experimental data are characterized by a rapid initial uptake of vapour followed by a slow down to final equilibrium or a slightly sigmoidal approach to final equilibrium. The diffusion–relaxation model provides a good approximation for the other two models when ψ is small, i.e. the two-stage sorption prevails; however, it is not applicable to the situation when ψ is larger than or close to unity, i.e. the characteristic diffusion time is longer than or comparable to the characteristic relaxation time. Both the variable surface-concentration model and the diffusion–reaction model are derived from the differential mass balance of penetrant with similar boundary conditions; however, the diffusion–reaction model takes internal relaxation into consideration for better physical significance, but its analytic solution is more complicated. The diffusion–reaction model also suggests that the apparent or measured diffusion coefficient may be lower than a 'true' one if a polymer possesses a large number of 'sites or holes' for penetrant to reside in or functional groups to immobilize the penetrant even if the exchange rate between the immobilized molecules and mobile ones is very fast and Fickian-like sorption is observed. From the fitted values of the diffusion coefficient (D_o), relaxation/reaction time constant (k), and the equilibrium ratio constant (ϕ) or the distribution coefficient ($K, K = (1 - \phi)/\phi$), they may depend on the state of the polymer or the concentration or activity of the penetrant. A natural extension of this work may assume history-dependent diffusion coefficient, rate constant, or ratio constant in the models for better correlation with the experimental data.

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REFERENCES

1 Fujita, H. *Portschr. Hochpolym.-Forsch.* 1961, **3**, 1
2 Park, G. S. 'Diffusion of Polymers' (Eds J. Crank and G. S. Park), Academic Press, London, 1968, Chap. 5, pp. 141–163
3 Frish, H. L. *Polym. Eng. Sci.* 1980, **20**, 1
4 Vrentas, J. S., Jarzebski, C. M. and Duda, J. L. *AIChE J.* 1975, **21**, 894
5 Vrentas, J. S. and Duda, J. L. *J. Polym. Sci., Polym. Phys. Edn* 1977, **15**, 441
6 Vrentas, J. S. and Duda, J. L. *AIChE J.* 1979, **25**, 1
7 Long, F. A. and Richman, D. *J. Am. Chem. Soc.* 1960, **82**, 513
8 Berens, A. R. and Hophenberg, H. B. *Polymer* 1978, **19**, 489
9 Joshi, S. and Astarita, G. *Polymer* 1979, **20**, 455
10 Kang, Y. S., Meldon, J. H. and Sung, N. *J. Polym. Sci., Polym. Phys. Edn* 1990, **28**, 1093
11 Vrentas, J. S. and Duda, J. L. 'Encyclopedia of Polymer Science and Engineering' (Eds H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges and J. I. Kroschwitz), 2nd Edn, Wiley, New York, 1985–1990, Vol. 5, pp. 36–68
12 Sanopoulou, M., Roussis, P. P. and Petropoulos, J. H. *J. Polym. Sci., Polym. Phys. Edn* 1995, **33**, 993
13 Bagley, E. and Long, F. A. *J. Am. Chem. Soc.* 1955, **77**, 2172
14 Newns, A. C. *Trans. Faraday Soc.* 1956, **52**, 1533
15 Kishimoto, A. and Kitahara, T. *J. Polym. Sci., A-1* 1967, **5**, 2147
16 Sun, Y.-M. and Lee, H.-L. *Polymer* 1996, **37**, 3915
17 Lee, H.-L., M.S. Thesis, Yuan-Ze Institute of Technology, Chung-Li, 1993
18 Crank, J. 'The Mathematics of Diffusion', 2nd Edn, Oxford University Press, London, 1975, Chap. 14
19 Vieth, W., Douglas, A. S. and Bloch, R. *J. Macromol. Sci.-Phys.* 1969, **B3**, 737
20 Tshudy, J. and Frankenberg, C. V. *J. Polym. Sci., Polym. Phys. Edn* 1973, **11**, 2027
21 Cohen, D. S. *J. Polym. Sci., Polym. Phys. Edn* 1983, **21**, 2057
22 IMSL, Inc., 'User's Manual: Math/library, Ver. 2', 1991, pp. 1017–1120
23 Berens, A. R. 'Barrier Polymers and Structures' (Ed. W. J. Koros), *ACS Symp. Ser.* No. 423, American Chemical Society, Washington, DC, 1990, Chap. 4, pp. 92–110
24 Richman, D. and Long, F. A. *J. Am. Chem. Soc.* 1960, **82**, 500
25 Best, M., Halley, J. W., Johnson, B. and Valles, J. L. *J. Appl. Polym. Sci.* 1993, **48**, 319