

# Numerical Examination of the Dual-Mode Sorption Model for Sorption Rate Experiments with an Extension for a Mobile Langmuir Component

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## Synopsis

Numerical methods were applied to the dual-mode sorption model for sorption rate experiments with an immobilized Langmuir component over broad ranges of polymer characteristics and experimental conditions. The variation of the diffusion coefficient evaluated using a single scaling procedure was examined. The numerical procedure was also applied to the model for infinite volume sorption and to sorption allowing for mobility of the Langmuir component of the penetrant.

## INTRODUCTION

The dual-mode sorption model (DMSM) has been successful in describing the sorption and permeation behavior of penetrant-polymer systems below the glass transition temperature.<sup>1-4</sup> It is based on a two-term sorption isotherm. In its simplest form, one term utilizes a Henry law dependence of the concentration on the penetrant pressure and the other a Langmuir dependence:

$$C = C_D + C_H = k_D p + \frac{C'_H b p}{1 + b p} \quad (1)$$

Vieth and Sladek<sup>5</sup> developed the model for the finite-volume sorption rate experiment under the constraint that the penetrant fraction attributed as the Langmuir component is completely immobilized, but in local equilibrium with the Henry law dissolution component. A sorption rate master curve was derived by numerical methods to allow investigators to estimate the diffusion coefficient by scaling sorption rate data to the master curve regardless of the values of the system parameters.

The model has been extended to include permeation with immobility of the Langmuir component,<sup>6</sup> permeation with mobility of the Langmuir component,<sup>7</sup> activity coefficient considerations,<sup>7,8</sup> replacement of the Henry law term with a nonlinear term for the dissolution component,<sup>9</sup> and the coupling of the two sorption modes.<sup>10</sup> Numerical methods have also been applied to permeation systems to obtain characteristics other than those provided by the closed-form

asymptotic solutions that have been useful in obtaining diffusion coefficients. For example, Toi et al.<sup>11</sup> obtained numerical solutions of the diffusion equation for permeation rate experiments and used them to analyze experimental data. The concentration dependence of apparent diffusion coefficients obtained in sorption rate experiments has also been analyzed to yield diffusion coefficients for both sorption modes in dual-mobility systems.<sup>12,13</sup> However, the extensions have apparently not included numerical solutions for sorption experiments with mobility of the Langmuir component. Numerical methods were used in this work to examine the DMSM applied to sorption rate experiments with plane slab absorbers for both immobilized and mobilized Langmuir component systems.

### EXAMINATION OF THE DMSM FOR SORPTION RATE EXPERIMENTS WITH AN IMMOBILIZED LANGMUIR COMPONENT

Following Vieth and Sladek,<sup>5</sup> numerical solutions of eq. (2) were obtained using the boundary conditions in eqs. (3)–(6) for finite-volume sorption rate experiments with plane slab absorbers and sorption rate master curves were produced.

$$\frac{\partial^2 C_D}{\partial X^2} = \left[ 1 + \frac{K}{(1 + bp)^2} \right] \frac{\partial C_D}{\partial \theta} \quad (2)$$

$$\theta = 0, \quad 0 \leq X \leq 1, \quad C_D = 0 \quad (3)$$

$$X = 0, \quad \theta \geq 0, \quad \frac{\partial C_D}{\partial X} = 0 \quad (4)$$

$$X = 1, \quad \theta > 0, \quad C_D = k_D p \quad (5)$$

$$p = p_0 - \left( \frac{RTL}{22,400a} \right) \int_0^1 (C_D + C_H) dx \quad (6)$$

$$\theta = \frac{tD}{L^2}, \quad K = \frac{C_H b}{k_D}, \quad X = \frac{x}{L} \quad (7)$$

The explicit method of solution was used.<sup>14</sup> The program allows for a preexperiment equilibrium pressure ( $p_I$ ) other than zero to be used in experiments initiated by an initial pressure ( $p_0$ ) so that interval as well as integral sorption experiments can be analyzed. The solution is expressed in terms of reduced variables  $\Phi$  and  $\theta'$  where

$$\Phi = \frac{p_0 - p}{p_0 - p_F} \quad (8)$$

$$\theta' = \frac{\theta}{\Gamma} = \frac{Dt}{L^2 \Gamma} \quad (9)$$

$$\Gamma = 1 + \frac{K}{(1 + bp)^2} \quad (10)$$

and the curves of  $\Phi$  versus  $\sqrt{\theta'}$  were produced. These are the master curves described by Vieth and Sladek. The diffusion coefficient  $D$  is determined by plotting  $\Phi$  versus  $\sqrt{(t/L^2)\Gamma}$ . The scaling factor required to superimpose the experimentally determined  $\Phi$  versus  $\sqrt{(t/L^2)\Gamma}$  curve on the master curve is  $\sqrt{D}$ .

As a test of the numerical procedure, curves of  $\Phi$  vs.  $\sqrt{\theta'}$  were calculated for the three sets of parameters used by Vieth and Sladek (VS) to establish their master curve, given in Table I. The value of  $\sqrt{\theta'}$  at  $\Phi = 0.5$ , i.e.,  $\sqrt{(\theta')_{1/2}}$ , has a spread of 0.038; approximately the same as the spread of the curves used to establish the VS master curve.<sup>5</sup> To examine further the range of master curves produced by this procedure, the effects of variation of the parameters  $k_D$ ,  $C'_H$ ,  $b$ , and  $L/a$  on the graph of  $\Phi$  vs.  $\sqrt{\theta'}$  were determined. Using the values of  $k_D$ ,  $C'_H$ , and  $b$  of solution in Table I and for double and half these values, the spread in  $\sqrt{(\theta')_{1/2}}$  increased to 0.083.

The effect of the displacement of the master curves on the value of  $D$  obtained by scaling the experimental curve is readily estimated.  $D$  is related to the value of  $\theta'$  of the master curve at  $\Phi = 0.5$ , i.e.,  $(\theta')_{1/2}$ , to the value of  $t/L^2$  of the experimental curve at  $(t/L^2)_{1/2}$  by

$$D = \frac{(\theta')_{1/2}\Gamma}{(t/L^2)_{1/2}} \tag{11}$$

The ratio of  $D$  calculated by scaling the experimental  $(t/L^2)_{1/2}$  to the  $(\theta')_{1/2}$  calculated using the DMSM parameters for the experiment ( $D$ ) to the  $D$  calculated by scaling to the  $(\theta')_{1/2}$  of the Vieth and Sladek master curve ( $D_{VS}$ ) is given by

$$\frac{D}{D_{VS}} = \frac{(\theta')_{1/2}}{(\theta'_{VS})_{1/2}} \tag{12}$$

The effects of changes in the DMSM parameters on the values of  $D_i/D_{VS}$  are illustrated in Table II for solution 2.

The master curves are more sensitive to  $L/a$  than the other sorption parameters. Master curves were calculated with the sorption parameters of solution 2, with the exception that  $L/a$  was varied from 0.111 and 0.888. The resulting curves are plotted in Figure 1. Significant errors would result if the VS curve

TABLE I  
DMSM Parameters Used to Calculate  $\Phi$  vs.  $\sqrt{\theta'}$  Master Curves at  $T = 313\text{ K}^a$

Solution	$C'_H$	$b$	$k_D$	$L/a$	$p_I$	$p_0$	$F$
1	5.3	0.44	0.38	0.333	0.0	1.0	0
2	5.3	0.35	0.67	0.333	0.0	1.0	0
3	5.3	0.50	0.15	0.518	0.0	1.0	0

<sup>a</sup> Used by Vieth and Sladek.<sup>5</sup> The units are as follows:  $C'_H = \text{cm}^3 \text{ gas (STP)/cm}^3 \text{ polymer}$   $b = \text{atm}^{-1}$ ,  $k_D = \text{cm}^3 \text{ gas (STP)/cm}^3 \text{ polymer atm}$ ,  $L/a = \text{dimensionless}$   $p_I = \text{atm}$ ,  $p_0 = \text{atm}$ ,  $F = \text{dimensionless}$ .

was used for experiments utilizing  $L/a$  values appreciably different from the values used for determining the VS curve. Considering the extremes, the ratio of  $D$  obtained using the master curve for  $L/a = 0.111$  to the  $D$  obtained using the master curve for  $L/a = 0.888$  is 3.6.

The effect of varying  $p_I$  and  $p_0$  on the master curve was investigated by calculating master sorption rate curves using the sorption parameters given for solution 1 with  $p_0$  changing from 0.1 to 2.0 and  $p_I = 0.0$ , and with  $p_0 = 1.0$  and  $p_I = 0.25, 0.50, \text{ and } 0.75$ . The ratios of  $D$  estimated by the several master curves to the  $D$  estimated by the original VS master curve, using  $(\theta')_{1/2}$  values in both cases, for  $p_I = 1.0$  and  $p_0 = 0.1, 0.5, \text{ and } 2.0$  are 0.68, 0.81, and 1.38. However, no displacement in the curves results from changing  $p_I$  while using a constant  $p_0$ .

The conclusion from these evaluations of the constancy of the master curves is that significant errors in  $D$  can be realized if determined by scaling to a single master curve, e.g., the VS master curve, when the sorption parameters differ significantly from those used in calculating the master curve. The results suggest that either numerical curve fitting procedures or master curves calculated for the specific experimental sorption parameters be used to obtain reliable diffusion coefficients.

### EXTENSION OF THE DMSM TO INFINITE-VOLUME SORPTION EXPERIMENTS

The master curve calculation procedure was altered to accommodate infinite-volume sorption experiments, i.e.,  $L/a \rightarrow 0$ . The experimental quantity of interest in this limit becomes the ratio ( $M$ ) of the concentration of penetrant in the polymer at time  $t$  ( $C$ ) to the equilibrium concentration at large  $t$  ( $C_F$ ), i.e.,  $M = C/C_F$ . Again, master curves of  $M$  versus  $\sqrt{\theta'}$  for the three solutions in Table II, with  $L/a = 0.0$  were calculated. They were essentially superimposable. To further examine the effects of the sorption parameters,  $C'_H$ ,  $k_D$ , and  $b$  were varied in the same manner as in Table II. The dependence of  $(\theta')_{1/2}$  on the

TABLE II  
Dependence of  $D_i/D_{VS}$  on Changes in Values of the DMSM Parameters,  $C'_H$ ,  $b$ ,  $k_D$ , and  $L/a^a$

Altered parameter	$D_i/D_{VS}$
None	1.00
$2L/a$	0.53
$L/2a$	1.44
$2b$	0.95
$b/2$	1.12
$k_D/2$	1.16
$2k_D$	0.78
$C'_H/2$	1.22
$2C'_H$	0.70

<sup>a</sup> Base values are  $C'_H = 5.3 \text{ cm}^3 \text{ gas (STP)/cm}^3 \text{ polymer}$ ,  $b = 0.35 \text{ atm}^{-1}$ ,  $k_D = 0.67 \text{ cm}^3 \text{ gas (STP)/cm}^3 \text{ polymer atm}$ , and  $L/a = 0.333$ .

sorption parameters is somewhat less than that found for the finite-volume calculation, 0.057 compared to 0.083, and in the opposite direction with respect to increasing the parameters. The use of a single master curve obtained for infinite-volume experiments would be more reliable in estimating  $D$  than for the finite-volume experiments.

### EXTENSION OF THE DMSM TO INCLUDE MOBILITY OF THE LANGMUIR COMPONENT IN SORPTION RATE MEASUREMENTS

The DMSM has been extended to include the mobility of the Langmuir component of the penetrant in permeation experiments. Frish<sup>15</sup> obtained asymptotic analytical solutions of the diffusion equation expressed in terms of penetrant concentrations for permeation experiments in the limits of high and low pressures. Paul and Koros<sup>7</sup> developed the solutions further and used them to analyze permeation experiments involving mobility of the Langmuir component. Solutions of the diffusion equation in terms of the penetrant chemical potential have been achieved by Petropoulos.<sup>8</sup>

The formulations used to obtain numerical solutions of the diffusion equations for sorption rate experiments that include mobility of the penetrant Langmuir component are provided in eqs. (13)–(17). The formulations and symbols follow Paul and Koros.<sup>7</sup> The penetrant flux is composed of two components.

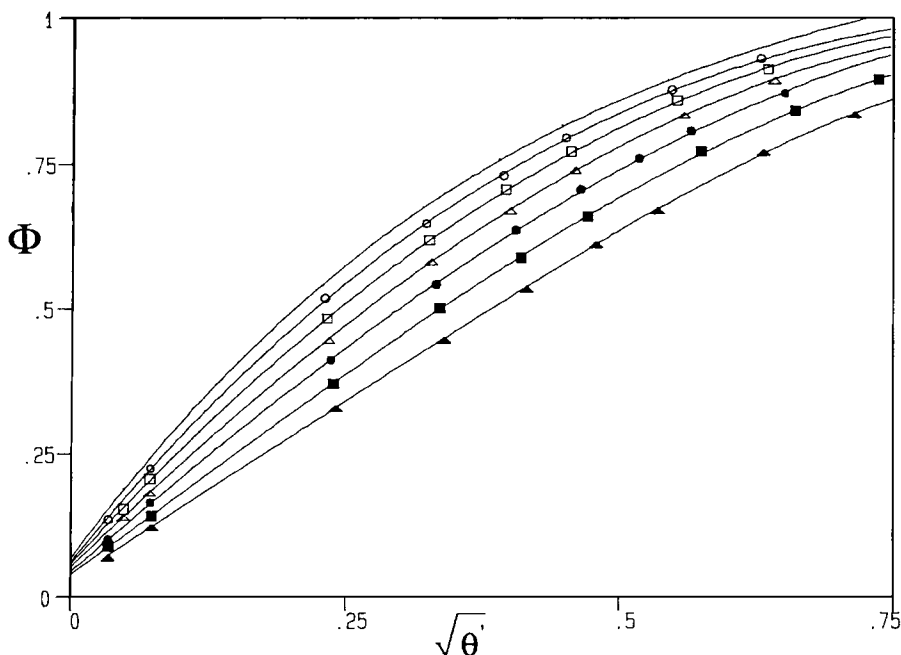


Fig. 1.  $\Phi$  vs.  $\sqrt{\theta}$  curves calculated for solution 2 parameters on  $L/a$ :  $\blacktriangle$   $L/a = 0.111$ ;  $\blacksquare$   $L/a = 0.222$ ;  $\bullet$   $L/a = 0.333$ ;  $\triangle$   $L/a = 0.444$ ;  $\square$   $L/a = 0.555$ ;  $\circ$   $L/a = 0.666$ ;  $/$   $L/a = 0.777$ .

$$J = -D_D \left( \frac{\partial C_D}{\partial x} \right) - D_H \left( \frac{\partial C_H}{\partial x} \right) \quad (13)$$

Setting

$$F = \frac{D_H}{D_D} \quad D_F = D_D \quad (14)$$

eq. (13) becomes

$$J = -D_F \left\{ 1 + \frac{\left[ 1 + \frac{KF}{(1+bp)^2} \right]}{\left[ 1 + \frac{K}{(1+bp)^2} \right]} \right\} \frac{\partial C}{\partial x} \quad (15)$$

and  $\theta'$  becomes  $\theta'_F$  with

$$\theta'_F = \frac{\theta}{\Gamma_F} = \frac{D_F t}{L^2 \Gamma_F} \quad (16)$$

and

$$\Gamma_F = \frac{\left[ 1 + \frac{K}{(1+bp)^2} \right]}{\left[ 1 + \frac{KF}{(1+bp)^2} \right]} \quad \frac{\Gamma}{\Gamma_F} = 1 + \frac{KF}{(1+bp)^2} \quad (17)$$

Numerical procedures similar to those used for the solutions with  $F = 0^{14}$  were applied using the boundary conditions listed in eqs. (3)–(6).

The effect of  $F$  on the master curves was examined. Curves of  $\Phi$  vs.  $\sqrt{\theta'_F}$ , again using the parameters for solution 2 given by Vieth and Sladek,<sup>5</sup> produced the spread in  $\sqrt{(\theta'_F)_{1/2}}$  of 0.037 for  $0 \leq F \leq 1$ .

The use of the model requires the determination of both  $D_F$  and  $F$ , i.e.,  $D_H$  and  $D_D$ . This can be accomplished using sorption rate data obtained for at least two experiments carried out at different  $p_0$ 's. Results from  $N$  experiments give  $N$  values of  $(t_i/L^2)_{1/2}$ ,  $i = 1, 2, \dots, N$ , using only the values at  $\Phi = 0.5$  for illustrative purposes. A graphic procedure involves using the master curve for  $F = 0$  to calculate a  $D_i$  for each experiment by scaling at  $\Phi = 0.5$ . These  $D_i$  would decrease with increasing  $p_{1/2}$  unless  $F = 0$ . The ratio  $D_i/D_F$  for each experiment is given from eqs. (9) and (17) as

$$\frac{D_i}{D_F} = \frac{\Gamma_i}{\Gamma_F} = 1 + \frac{KF}{(1+bp_i)^2} \quad (18)$$

where  $D_F$  and  $F$  are constant for the series of experiments and  $(\theta'_i/\theta'_F)$  is assumed to be 1; and is in fact  $1.00 \pm 0.06$  for the parameters of solution 2. Using only the values at  $\Phi = 0.5$  as an example yields

$$\frac{D_i}{D_F} = \frac{(\Gamma_i)_{1/2}}{(\Gamma_F)_{1/2}} = 1 + \frac{KF}{[1 + b(p_i)_{1/2}]^2} \tag{19}$$

By selecting values of  $F$  until  $D_F$  becomes constant for the series of experiments, both  $D_F$  and  $F$  are determined.

As an example of the sensitivity of the ratio of  $D_i/D_F$  values of the ratio calculated by eq. (19) for parameters of solution 1 given by Vieth and Skadek<sup>5</sup> are plotted as a function of  $p_{1/2}$  for selected values of  $F$  in Figure 2. The variation of the dependence of  $D_i/D_F$  versus  $p_{1/2}$  on  $F$  appears to be large enough for these parameters to provide a means of estimating  $D_F$  and  $F$ . The sensitivity of the method would decrease as  $K$  and  $b$  decrease. This procedure offers a simple means of estimating  $D_F$  and  $F$  from sorption rate experiments, at least when the parameters  $K$  and  $b$  have appropriate values. By conducting experiments to a  $p_{1/2}$  high enough to obtain the limit  $D_i \rightarrow D_F$ , it would be necessary to determine only an average  $F$  for the experiments by eq. (19). In some systems this might not be possible and the curve fitting procedure could be used.

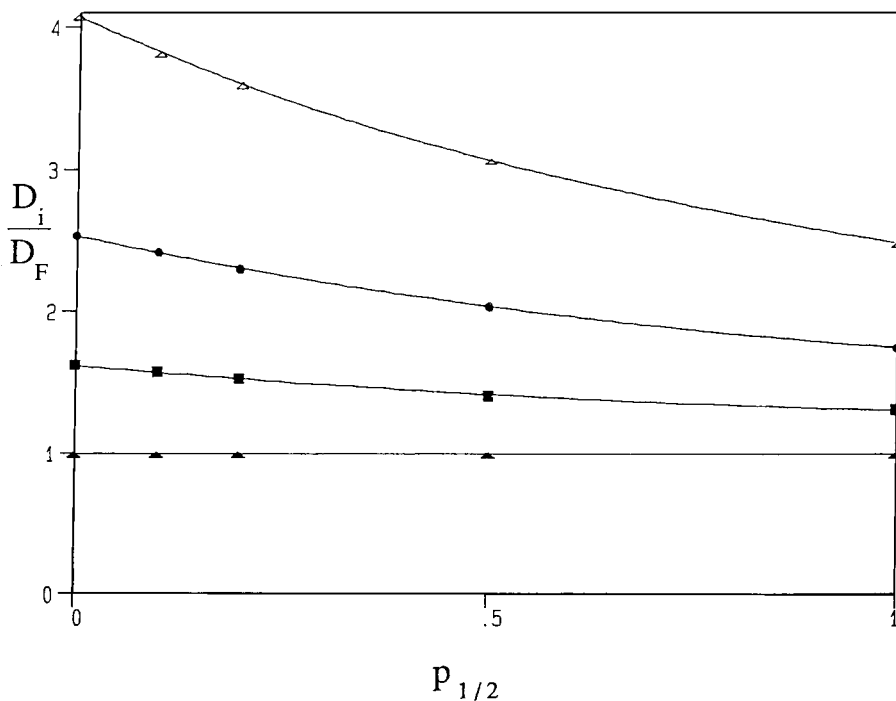


Fig. 2.  $D_i/D_F$  vs.  $p_{1/2}$  for parameters  $K = 6.14$  and  $b = 0.44$  (Solution 1, Vieth and Skadek<sup>5</sup>) and selected values of  $F$ :  $\blacktriangle$   $F = 0.0$ ;  $\blacksquare$   $F = 0.1$ ;  $\bullet$   $F = 0.25$ ;  $\triangle$   $F = 0.50$ .

### Nomenclature

$a$	Distance representative of the volume contacting the face of the film; volume contacting one surface of the film is the area of membrane multiplied by the distance $a$ , cm
$A$	Film surface area, $\text{cm}^2$
$b$	Langmuir affinity constant, $\text{atm}^{-1}$
$C$	Total penetrant concentration in polymer, $\text{cm}^3 \text{ gas (STP)}/\text{cm}^3 \text{ polymer}$
$C_D$	Henry's law dissolution component concentration, $\text{cm}^3 \text{ gas (STP)}/\text{cm}^3 \text{ polymer}$
$C_H$	Langmuir component concentration, $\text{cm}^3 \text{ gas (STP)}/\text{cm}^3 \text{ polymer}$
$C'_H$	Langmuir saturation constant, $\text{cm}^3 \text{ gas (STP)}/\text{cm}^3 \text{ polymer}$
$D$	Diffusion coefficient, $\text{cm}^2/\text{s}$
$D_D$	Diffusion coefficient of the Henry law component, $\text{cm}^2/\text{s}$
$D_H$	Diffusion coefficient of the Langmuir component, $\text{cm}^2/\text{s}$
$k_D$	Henry's law constant, $\text{cm}^3 \text{ gas (STP)}/\text{cm}^3 \text{ polymer atm}$
$F$	Ratio of the diffusion coefficient of the Langmuir component to the diffusion coefficient of the Henry law component
$K$	Defined by eq. (6)
$L$	Half thickness of the polymer sheet, cm
$L/a$	Ratio of the polymer film volume to the sorption cell volume
$M$	Ratio of the penetrant concentration at time $t$ to the equilibrium concentration in infinite volume sorption experiments
$p$	Penetrant pressure, atm
$p_I$	Penetrant pressure in equilibrium with polymer film prior to initiating the sorption experiment, atm
$p_0$	Penetrant pressure imposed to initiate the experiment, atm
$R$	Gas constant, $82.05 \text{ cm}^3 \text{ atm}/\text{mol K}$
$t$	Time, s
$T$	Temperature, K
$x$	Distance perpendicular to film surface, cm
$X$	Dimensionless distance, $X = x/L$
$\Gamma$	Defined by eq. (10)
$\Gamma_F$	Defined by eq. (17)
$\Phi$	Defined by eq. (8)
$\theta$	Dimensionless time; defined by eq. (7)
$\theta'$	Defined by eq. (9)
$\theta'_F$	Defined by eq. (16)

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Received April 21, 1989

Accepted November 20, 1989