

Errors associated with swelling in the analysis of polymer–solvent diffusion measurements

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Abstract

Sorption curves are generated from a mathematical model which includes the influence of the polymer swelling for unsteady-state sorption of a vapor or liquid by a polymer. To investigate the simultaneous effects of the specific volumes of the polymer–penetrant pair and the difference between the final and initial equilibrium concentrations on the sorption curves, statistical experimental design approach is used. Simulation results obtained from the numerical solution of model equations are utilized to estimate the error that would occur if one simply evaluates the diffusion coefficient using the traditional formulas derived from the analytical solution of the sorption equation. An empirical expression is developed that describes the effects of the difference between the final and initial equilibrium concentrations and the specific volumes of the polymer and the penetrant on the magnitude of error in diffusivity associated with the use of one of these traditional formulas so called the initial slope method. The predictive ability of the regression model is tested by performing additional simulations not used in the regression analysis.

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1. Introduction

Transport behavior of low molecular weight substances in polymers plays an important role in many industrial processes and in the application of polymers. In order to design and optimize such processes and many consumer products, knowledge of the diffusion coefficients within the polymer is required. Many of the experimental diffusivity data of low molecular weight compounds in the polymers are obtained with step-change sorption experiments (Vrentas and Vrentas, 1998a,b). For a differential step-change sorption experiment, mass of the penetrant per unit area that has entered a polymer film at time t , M_t , is measured continuously until sorption equilibrium is reached. The strong concentration dependence of diffusion coefficients for polymer–solvent systems as well as moving boundary effects are two important complications involved in the analysis of differential sorption

experiments. To eliminate such complexities, thus, to calculate single values of diffusion coefficients, the difference between the initial and final equilibrium concentrations of the penetrant is kept small. However, due to accuracy of the experimental sorption curves, many differential sorption experiments are obtained with significant step change (Vrentas and Vrentas, 2001). Recently, Alsoy and Duda (2002) have analyzed unsteady-state sorption of a vapor or liquid by a polymer to investigate the influence of the moving phase boundary associated with polymer swelling and diffusion-induced convection. They have utilized the simulation results to estimate the error that would occur if one of the common formulas so-called half time method is used to calculate the diffusivities from the differential sorption data. According to their analysis, the magnitude of error depends not only on the initial and equilibrium concentrations of the solvent but also on the specific volume of the polymer and solvent pair.

The objectives of this article are to: (a) compare the magnitude of errors that would occur if one simply evaluates the diffusion coefficient using the half time method or the initial

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slope method both of which are derived from the analytical solution of the sorption equation (Crank, 1975), (b) apply the statistical experimental design approach in order to determine simulation conditions, (c) derive an empirical expression to calculate the magnitude of error associated with the use of the initial slope method which is frequently used by practitioners.

2. Theory

The analysis of differential step-change sorption experiment is based on the following assumptions: (1) The sorption process is isothermal. (2) The gas phase is essentially pure and the liquid phase consists of a binary mixture of polymer and solvent. (3) There is no chemical reaction in the liquid phase. (4) There is no volume change on mixing, thus, the partial specific volumes of the polymer and solvent are independent of composition. (5) The diffusion process is a viscous Fickian diffusion process. (6) Pressure effects are negligible. (7) Equilibrium is established instantaneously at the polymer gas interface. (8) The mutual binary diffusion coefficient is considered to be independent of composition. Based on these assumptions, Duda and Vrentas (1968) have derived model equations in rectangular coordinate system using mass average velocity as a reference frame. The complexity of the three coupled model equations were reduced by utilizing different length and concentration variables and mass average reference frame (Duda and Vrentas, 1971). Alsoy and Duda (2002) used the Duda–Vrentas (1971) coordinate transformation in conjunction with defining the diffusive flux relative to volume average velocity to provide a single equation formulation. According to their formulation, the species continuity equations for the solvent denoted by 1 and polymer denoted by 2

$$\frac{\partial \rho_1}{\partial t} + \frac{\partial(\rho_1 v_1)}{\partial x} = 0, \quad (1)$$

$$\frac{\partial \rho_2}{\partial t} + \frac{\partial(\rho_2 v_2)}{\partial x} = 0 \quad (2)$$

are converted to the following equation:

$$\left(\frac{\partial q_1}{\partial t}\right)_{\xi} + \left(\frac{\partial j_1^0}{\partial \xi}\right)_t = 0 \quad (3)$$

after introducing a diffusive flux $j_1^0 = \rho_1(v_1 - v_2)$, a new concentration variable, $q_1 = \rho_1/\rho_2 \hat{V}_2$, and a new length variable $\xi(x, t) = \int_0^x \rho_2 \hat{V}_2 dx$. If diffusive flux is expressed in terms of the new length and concentration variables,

$$j_1^0 = D(\rho_2 \hat{V}_2)^2 \quad (4)$$

and is substituted into Eq. (3), the sorption process is described by the following equation:

$$\left(\frac{\partial q_1}{\partial t}\right)_{\xi} = \frac{\partial}{\partial \xi} \left[D(\rho_2 \hat{V}_2)^2 \frac{\partial q_1}{\partial \xi} \right]. \quad (5)$$

Table 1
Specific volumes of the polymers and solvents

Component	Specific volume (cm ³ /g)
Carbon tetrachloride	0.63
Chloroform	0.67
Vinyl acetate	1.08
Toluene	1.16
Tetrahydrofurane	1.14
Ethyl benzene	1.16
Poly-4-methylpentene-1	1.2
Low density polyethylene	1.09
Polymethyl methacrylate	0.85
Polyimide	0.7
Polyvinyl chloride	0.65

Eq. (5) is a nonlinear equation which is subject to the following initial and boundary conditions:

$$\left(\frac{\partial q_1}{\partial \xi}\right)_{\xi=0} = 0, \quad q_1(\xi_L, t) = q_{1E}, \quad q_1(\xi, 0) = q_{10}, \quad (6)$$

$$\xi_L = \rho_{20} \hat{V}_2 L.$$

The solution of Eqs. (5) and (6) gives concentration of solvent in the polymer as a function of position and time. When integrated, these data can be used to calculate the sorption uptake curve which is defined as the ratio of amount of penetrant absorbed by the polymer at any time t , M_t , to the amount absorbed when equilibrium is reached, M_{∞} . The predicted uptake curves can then be utilized to estimate the magnitude of error that would occur if the diffusion coefficient is calculated from two traditional approaches, the half time method or initial slope method. Both methods are derived from the analytical solution of the mass transfer problem with a Fickian constitutive equation and negligible diffusion-induced convection and moving boundary effects. In the initial slope method, the diffusion coefficient is deduced from an observation of the initial gradient of a graph of M_t/M_{∞} as a function of \sqrt{t} . If the upper surface of a polymer sheet of thickness L is exposed to the penetrant while its lower surface is impermeable, fractional uptake curve is given by (Crank, 1975)

$$\frac{M_t}{M_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \times \exp \left[-\frac{D(2m+1)^2 \pi^2 t}{L^2} \right], \quad (7)$$

where at small times as $t \rightarrow 0$ it is simplified as follows:

$$\frac{M_t}{M_{\infty}} = \frac{2}{\sqrt{\pi}} \left[\frac{Dt}{L^2} \right]^{1/2}. \quad (8)$$

If dimensionless time is defined as $t^* = Dt/L^2$ it is clear from Eq. (8) that the curve of M_t/M_{∞} against $\sqrt{t^*}$ yields a value of slope, $2/\sqrt{\pi}$. This slope is the same for all systems where diffusion coefficient is constant as well as polymer swelling

Table 2
Values of the parameters in 4^3 factorial design

Set I			Set II			Set III			Set IV						
Run #	\hat{V}_1	\hat{V}_2	$\Delta\omega_{1E}$	Run #	\hat{V}_1	\hat{V}_2	$\Delta\omega_{1E}$	Run #	\hat{V}_1	\hat{V}_2	$\Delta\omega_{1E}$	Run #	\hat{V}_1	\hat{V}_2	$\Delta\omega_{1E}$
1	0.6	0.6	0.01	17	0.6	0.6	0.173	33	0.6	0.6	0.336	49	0.6	0.6	0.5
2	0.8	0.6	0.01	18	0.8	0.6	0.173	34	0.8	0.6	0.336	50	0.8	0.6	0.5
3	1.0	0.6	0.01	19	1.0	0.6	0.173	35	1.0	0.6	0.336	51	1.0	0.6	0.5
4	1.2	0.6	0.01	20	1.2	0.6	0.173	36	1.2	0.6	0.336	52	1.2	0.6	0.5
5	0.6	0.8	0.01	21	0.6	0.8	0.173	37	0.6	0.8	0.336	53	0.6	0.8	0.5
6	0.8	0.8	0.01	22	0.8	0.8	0.173	38	0.8	0.8	0.336	54	0.8	0.8	0.5
7	1.0	0.8	0.01	23	1.0	0.8	0.173	39	1.0	0.8	0.336	55	1.0	0.8	0.5
8	1.2	0.8	0.01	24	1.2	0.8	0.173	40	1.2	0.8	0.336	56	1.2	0.8	0.5
9	0.6	1.0	0.01	25	0.6	1.0	0.173	41	0.6	1.0	0.336	57	0.6	1.0	0.5
10	0.8	1.0	0.01	26	0.8	1.0	0.173	42	0.8	1.0	0.336	58	0.8	1.0	0.5
11	1.0	1.0	0.01	27	1.0	1.0	0.173	43	1.0	1.0	0.336	59	1.0	1.0	0.5
12	1.2	1.0	0.01	28	1.2	1.0	0.173	44	1.2	1.0	0.336	60	1.2	1.0	0.5
13	0.6	1.2	0.01	29	0.6	1.2	0.173	45	0.6	1.2	0.336	61	0.6	1.2	0.5
14	0.8	1.2	0.01	30	0.8	1.2	0.173	46	0.8	1.2	0.336	62	0.8	1.2	0.5
15	1.0	1.2	0.01	31	1.0	1.2	0.173	47	1.0	1.2	0.336	63	1.0	1.2	0.5
16	1.2	1.2	0.01	32	1.2	1.2	0.173	48	1.2	1.2	0.336	64	1.2	1.2	0.5

Table 3
Relative errors in diffusivities determined from the initial slope and the half time methods^a

Set I			Set II			Set III			Set IV		
Run #	Initial slope	Half time	Run #	Initial slope	Half time	Run #	Initial slope	Half time	Run #	Initial slope	Half time
1	0.931	-1.521	17	11.589	-28.214	33	23.398	-71.681	49	36.671	-153.80
2	0.996	-1.958	18	14.743	-37.986	34	28.606	-98.228	50	42.966	-216.08
3	1.202	-2.936	19	17.641	-48.051	35	33.051	-126.37	51	47.996	-284.05
4	1.560	-2.833	20	20.315	-58.261	36	36.895	-155.84	52	52.127	-357.57
5	0.627	-1.229	21	9.03	-20.920	37	18.85	-52.573	53	30.673	-110.63
6	0.786	-1.521	22	11.589	-28.214	38	23.398	-71.681	54	36.637	-153.81
7	0.944	-1.812	23	13.979	-35.507	39	27.384	-91.518	55	41.524	-200.04
8	1.10	-2.104	24	16.222	-42.946	40	30.913	-112.08	56	45.616	-249.34
9	0.531	-0.937	25	7.409	-16.690	41	15.797	-41.487	57	26.406	-86.267
10	0.659	-1.229	26	9.556	-22.379	42	19.811	-56.365	58	31.970	-119.09
11	0.786	-1.521	27	11.588	-28.214	43	23.398	-71.681	59	36.637	-153.80
12	0.912	-1.812	28	13.513	-34.048	44	26.626	-87.433	60	40.618	-190.56
13	0.620	-0.791	29	6.287	-13.919	45	13.602	-34.339	61	23.263	-70.659
14	0.574	-1.083	30	8.134	-18.587	46	17.187	-46.446	62	28.377	-96.915
15	0.68	-1.229	31	9.903	-23.4	47	20.436	-58.845	63	32.804	-124.629
16	0.931	-1.521	32	11.588	-28.214	48	23.398	-71.681	64	36.671	-153.80

^a% relative errors were calculated from Eqs. (9) and (11) using the simulation results.

and diffusion-induced convection are negligible. Thus, if the initial slope of uptake curves, IS, presented as M_t/M_∞ as a function of $\sqrt{t^*}$ are observed, then the magnitude of error in diffusivities obtained from the initial slope method can be easily estimated as follows:

$$\% \text{ Relative error in diffusivity} = \left(\frac{2/\sqrt{\pi} - IS}{2/\sqrt{\pi}} \right) 100. \quad (9)$$

In the half time method, diffusivity is calculated from (Crank, 1975)

$$D = \frac{0.1968}{(t/L^2)_{0.5}}. \quad (10)$$

It is obvious from Eq. (10) that if the polymer swelling is negligible and diffusivity is constant, then dimensionless time, t^* , should be equal to 0.1968 when $M_t/M_\infty = 0.5$. Consequently, the magnitude of error associated with the use of the half time method can be calculated from Eq. (11) by comparing the dimensionless time obtained from the simulation results when $M_t/M_\infty = 0.5$, $t_{0.5}^*$, with the corresponding value from the analytical solution, that is, 0.1968

$$\% \text{ Relative error in diffusivity} = \left(\frac{0.1968 - t_{0.5}^*}{0.1968} \right) 100. \quad (11)$$

3. Statistical design of simulations

In this study the statistical experimental design approach was applied to determine the simulation conditions since simulation can be considered as an experiment conducted on a computer. Statistical design of experiments refers to the process of planning the experiment so that data can be analyzed appropriately to draw meaningful conclusions. As a first step in the design of simulations, % relative errors in diffusivities calculated from Eqs. (9) and (11) were chosen as responses. The magnitude of error in diffusivities is

Table 4
Summary of the significance level of each factor

Factor	Sum of squares, SS	ω^2
A	617.1	0.046
B	651.6	0.048
C	11545.4	0.87
A × B	7.05	0.00053
A × C	251.9	0.019
B × C	258.5	0.019
A × B × C	2.38	0.00018

Table 5
Output from the statistical analysis of regression

R^2	0.9982
F value	3282.01
S_{ey}	0.671
SS _{Reg}	13310.3
SS _{Res}	24.33

Table 6
Input parameters of the simulations used to test the predictive ability of Eq. (14)

Set I				Set II				Set III				Set IV			
Run #	\hat{V}_1	\hat{V}_2	$\Delta\omega_{1E}$	Run #	\hat{V}_1	\hat{V}_2	$\Delta\omega_{1E}$	Run #	\hat{V}_1	\hat{V}_2	$\Delta\omega_{1E}$	Run #	\hat{V}_1	\hat{V}_2	$\Delta\omega_{1E}$
1	0.9	0.6	0.01	20	0.76	0.6	0.01	39	1.2	0.76	0.037	58	0.95	0.95	0.136
2	0.6	0.9	0.01	21	0.95	0.6	0.01	40	0.6	0.95	0.037	59	1.2	0.95	0.136
3	0.9	0.9	0.01	22	0.6	0.76	0.01	41	0.76	0.95	0.037	60	0.6	1.2	0.136
4	1.2	0.9	0.01	23	0.76	0.76	0.01	42	0.95	0.95	0.037	61	0.76	1.2	0.136
5	0.9	1.2	0.01	24	0.95	0.76	0.01	43	1.2	0.95	0.037	62	0.95	1.2	0.136
6	0.6	0.6	0.26	25	1.2	0.76	0.01	44	0.6	1.2	0.037	63	1.2	1.2	0.136
7	0.9	0.6	0.26	26	0.6	0.95	0.01	45	0.76	1.2	0.037	64	0.76	0.6	0.5
8	1.2	0.6	0.26	27	0.76	0.95	0.01	46	0.95	1.2	0.037	65	0.95	0.6	0.5
9	0.6	0.9	0.26	28	0.95	0.95	0.01	47	1.2	1.2	0.037	66	0.6	0.76	0.5
10	0.9	0.9	0.26	29	1.2	0.95	0.01	48	0.6	0.6	0.136	67	0.76	0.76	0.5
11	1.2	0.9	0.26	30	0.76	1.2	0.01	49	0.76	0.6	0.136	68	0.95	0.76	0.5
12	0.6	1.2	0.26	31	0.95	1.2	0.01	50	0.95	0.6	0.136	69	1.2	0.76	0.5
13	0.9	1.2	0.26	32	0.6	0.6	0.037	51	1.2	0.6	0.136	70	0.6	0.95	0.5
14	1.2	1.2	0.26	33	0.76	0.6	0.037	52	0.6	0.76	0.136	71	0.76	0.95	0.5
15	0.9	0.6	0.5	34	0.95	0.6	0.037	53	0.76	0.76	0.136	72	0.95	0.95	0.5
16	0.6	0.9	0.5	35	1.2	0.6	0.037	54	0.96	0.76	0.136	73	1.2	0.95	0.5
17	0.9	0.9	0.5	36	0.6	0.76	0.037	55	1.2	0.76	0.136	74	0.76	1.2	0.5
18	1.2	0.9	0.5	37	0.76	0.76	0.037	56	0.6	0.95	0.136	75	0.95	1.2	0.5
19	0.9	1.2	0.5	38	0.95	0.76	0.037	57	0.76	0.95	0.136				

influenced by the initial and equilibrium concentrations of the solvent as well as the specific volumes of the polymer and the solvent. A case in which polymer is initially free of penetrant was considered, thus, number of parameters influencing the error in diffusivities were reduced to three by setting initial concentration of solvent to zero. In the second step of the simulation design, simulation conditions were set within the following region: Equilibrium concentration of the solvent in terms of weight fraction, ω_{1E} , ranges from 0.01 to 0.5 while the specific volumes of the polymer, \hat{V}_2 , and the solvent, \hat{V}_1 , are changed from 0.6 to 1.2 cm³/g. The ranges for the specific volumes, \hat{V}_1 and \hat{V}_2 were chosen by searching the values for many polymers and solvents and

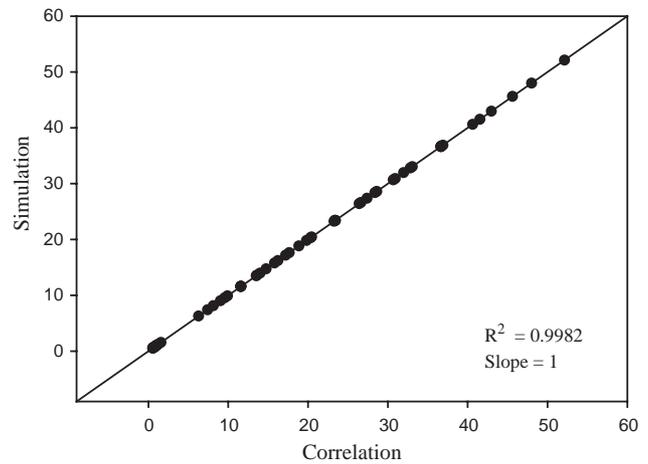


Fig. 1. Simulation data used in deriving Eq. (14) vs. theoretical values from Eq. (14) for the % relative error in diffusivity associated with the use of the initial slope method.

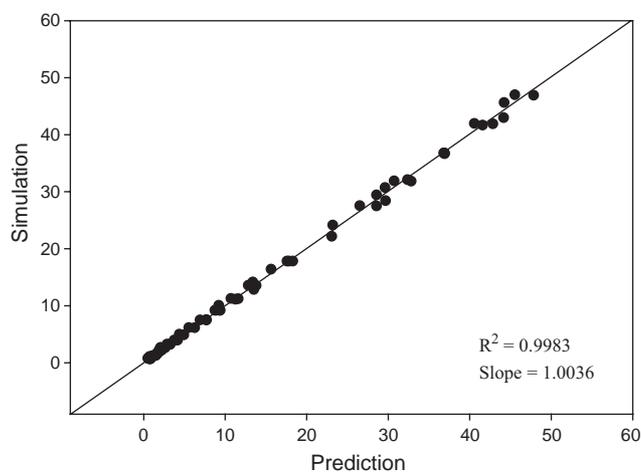


Fig. 2. Simulation data not used in deriving Eq. (14) vs. theoretical values from Eq. (14) for the % relative error in diffusivity associated with the use of the initial slope method.

some of these values were tabulated in Table 1 [Daubert and Danner, 1994; Progelhof and Throne, 1993]. For a step change differential sorption experiment, the ideal situation is to keep difference between the final and initial equilibrium concentrations as small as possible. For the statistical design of the simulations the minimum value for ω_{1E} was chosen as 0.01 since a smaller step size cannot be obtained even with new experimental devices having high resolution and accuracy. Many differential sorption experiments are obtained with significant step change. Based on this fact, the maximum value for ω_{1E} was chosen as 0.5. The step size of 0.5 may be high for some of the experimental cases. On the other hand, empirical expression developed in this study will cover many possible scenarios in order to estimate the magnitude of error in diffusivity associated with the use of the traditional initial slope method.

The simulation conditions were determined using a 4^3 factorial design in which all possible combinations of three

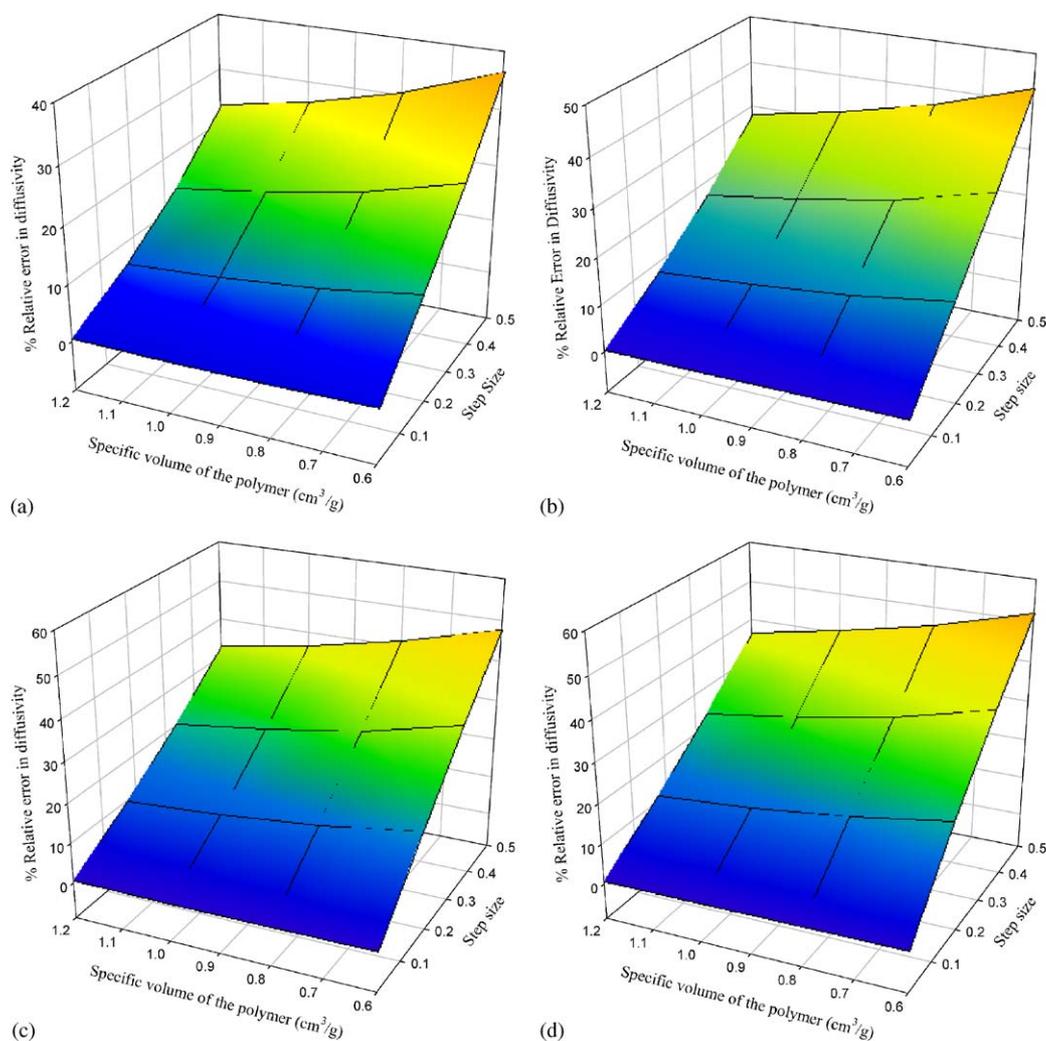


Fig. 3. The three-dimensional response surface plots highlighting the effects of the specific volume of the polymer and the step size on the % relative error in diffusivity associated with the use of the initial slope method: (a) $\hat{V}_1 = 0.6 \text{ cm}^3/\text{g}$, (b) $\hat{V}_1 = 0.8 \text{ cm}^3/\text{g}$, (c) $\hat{V}_1 = 1 \text{ cm}^3/\text{g}$, and (d) $\hat{V}_1 = 1.2 \text{ cm}^3/\text{g}$.

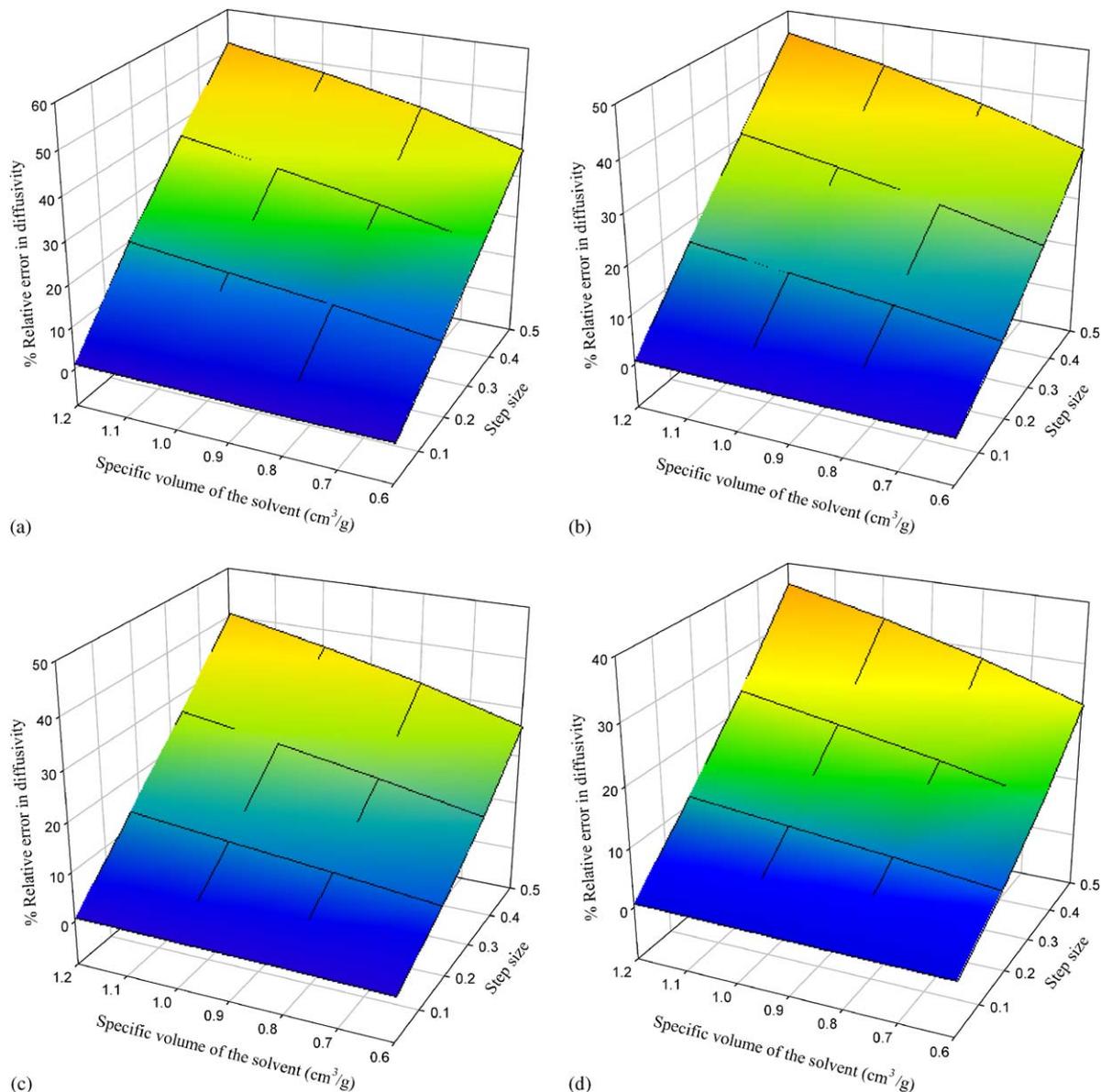


Fig. 4. The three-dimensional response surface plots highlighting the effects of the specific volume of the penetrant and the step size on the % relative error in diffusivity associated with the use of the initial slope method: (a) $\hat{V}_1 = 0.6 \text{ cm}^3/\text{g}$, (b) $\hat{V}_2 = 0.8 \text{ cm}^3/\text{g}$, (c) $\hat{V}_2 = 1 \text{ cm}^3/\text{g}$, and (d) $\hat{V}_2 = 1.2 \text{ cm}^3/\text{g}$.

parameters each at four levels were investigated (Montgomery, 2001). Thus, the total combinations of the levels of these three parameters are $4^3 = 64$. Factorial design is more efficient than one-factor-at-a-time approach and is necessary when interactions may be present to avoid misleading conclusions. In addition, factorial designs allow the effects of parameter to be estimated at several levels of the other parameters, yielding conclusions that are valid over a range of experimental conditions.

4. Statistical analysis

Significance level for a factor or factor interaction effect can be measured by an index Omega squared (ω^2). It is

defined as the ratio of the sum of squared deviation of a factor (SS) to the total sum of squared deviation (SS_T)

$$\omega^2 = \frac{SS}{SS_T}. \quad (12)$$

If factors A and B represent the specific volumes of the solvent and the polymer, respectively, while factor C represents the difference between the final and initial concentration of the solvent, the total sum of squared deviation can be expressed as follows:

$$SS_T = SS_A + SS_B + SS_C + SS_{A \times B} + SS_{A \times C} + SS_{B \times C} + SS_{A \times B \times C}. \quad (13)$$

Mathematical expressions required to calculate the sum of squared deviation of the main effects (SS_A , SS_B , SS_C) or

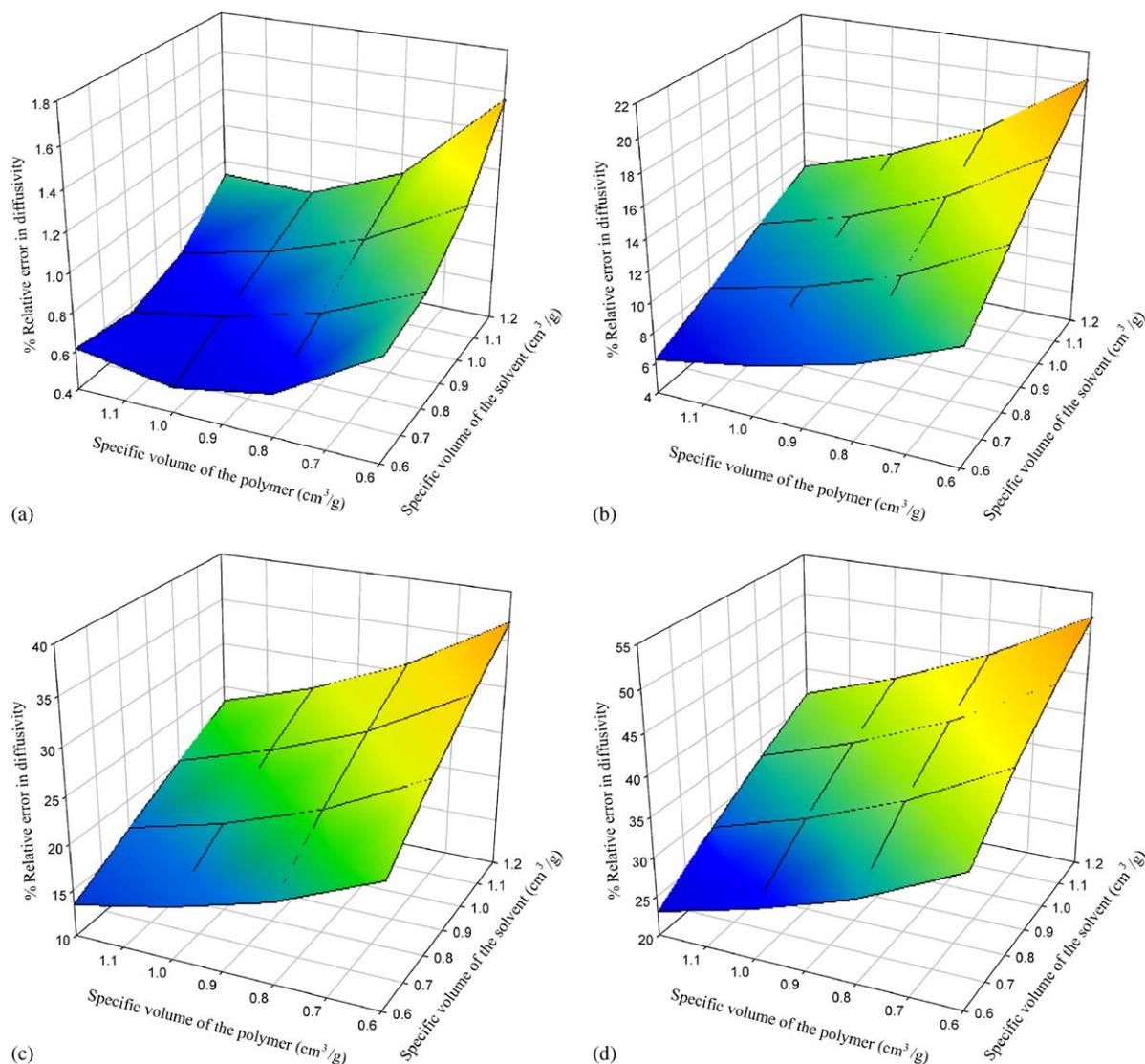


Fig. 5. The three-dimensional response surface plots highlighting the effects of the specific volumes of the polymer and the penetrant on the % relative error in diffusivity associated with the use of the initial slope method: (a) $\Delta\omega_{1E} = 0.01$, (b) $\Delta\omega_{1E} = 0.173$, (c) $\Delta\omega_{1E} = 0.336$, and (d) $\Delta\omega_{1E} = 0.5$.

the interaction effects ($SS_{A \times B}$, $SS_{A \times C}$, $SS_{B \times C}$, $SS_{A \times B \times C}$) can be found somewhere else (Myers, 1989).

5. Results and discussion

As noted above, the diffusion coefficients of penetrants in polymers are usually obtained by analyzing the experimental data taken with step change sorption experiments. The analysis is usually based on simple expressions, the half time and the initial slope method, derived from the analytical solution of the unsteady-state Fickian diffusion equation. The error in diffusivities associated with the use of these expressions is strongly influenced by the swelling of the polymer film. To investigate the effect of swelling on these errors, Eqs. (5) and (6) were solved numerically for the conditions

corresponding to the 4^3 factorial design shown in Table 2. By analyzing the uptake curves, the dimensionless initial slope, IS, and the half time, $t_{0.5}^*$, were determined and then % relative errors in diffusivities were calculated from Eqs. (9) and (11). The results are summarized in Table 3. As is evident from these results, the magnitude of error in diffusivities determined from the half time method is much larger than that computed from the initial slope method for all combinations of variables considered. This result is due to the fact that the assumption utilized in deriving Eq. (10) is more critical than the assumption used in obtaining Eq. (8). Simply, the use of Eq. (10) is limited for cases where the sorption curve, M_t/M_∞ , is linear up to 50 percent. However, in most cases the sorption curve is linear in the initial stages of the sorption process. Consequently, the initial slope method is more frequently used in determining the diffusivity of

the penetrants in polymers and the effects of factors on the magnitude of the error associated with the use of this method were determined.

Statistical analysis of the simulation results was performed in two steps. As a first step, significance level for a factor or factor interaction effect was measured by the criteria suggested by Cohen (1997). According to this criteria, the effect of a factor is considered to be small if the value of ω^2 is around 0.01, medium if it is around 0.06, and large if the factor produces an ω^2 value of 0.15 or greater. Table 4 lists ω^2 values of the main effects (ω_A^2 , ω_B^2 , ω_C^2) and the interaction effects ($\omega_{A \times B}^2$, $\omega_{A \times C}^2$, $\omega_{B \times C}^2$, $\omega_{A \times B \times C}^2$). The results in Table 4 clearly indicate that the most influential factor on the magnitude of the error in diffusivities is the difference between the equilibrium and the initial concentration of the solvent ($\omega_C^2 > 0.15$). Other main factors, the specific volume of the solvent and polymer have medium effects ($\omega_A^2 \sim 0.05$, $\omega_B^2 \sim 0.05$) while their interactions with factor C (the difference between the final and the initial concentration of the solvent) have small effects ($\omega_{A \times C}^2 \sim 0.02$, $\omega_{B \times C}^2 \sim 0.02$) on the magnitude of the error.

In the second step of the statistical analysis, the error data obtained from the initial slope method were fit by a quadratic polynomial using multiple regression analysis tool in Excel. As shown in Eq. (14), the resulting expression includes the effects of significant main and the interaction factors just mentioned above.

$$\begin{aligned} \text{\% Relative error in diffusivity} \\ = -5.07458 + 5.894974\hat{V}_1 + 5.906678\hat{V}_2 \\ + 67.6656\Delta\omega_{1E} - 6.5608\hat{V}_1\hat{V}_2 + 75.35612\hat{V}_1\Delta\omega_{1E} \\ - 78.0667\hat{V}_2\Delta\omega_{1E} + 12.11005\Delta\omega_{1E}^2 \\ - 54.1057\hat{V}_1\Delta\omega_{1E}^2 + 58.72984\hat{V}_2\Delta\omega_{1E}^2. \end{aligned} \quad (14)$$

In this equation, $\Delta\omega_{1E}$ represents the difference between the equilibrium and initial concentration of the solvent and is equal to the equilibrium weight fraction of the penetrant, ω_{1E} , since its initial concentration in the polymer is set to zero. The output from the regression analysis is summarized in Table 5. In most cases, the quality of the fitted model is determined by the coefficient of determination, often referred to, symbolically, as R^2 and interpreted as the proportion of variation in the response data that is explained by the model. R^2 value of 0.9982 close to 1 indicates that the fit of the regression model to the data is perfect. The F statistic or observed F value is viewed as a ratio that expresses variance explained by the model divided by variance due to model error or experimental error. Usually the observed F value is compared with the F -critical value to determine if the relationship between the dependent and independent variables occurs by chance. Large value of F (3282.01) which is substantially greater than the F -critical value determined as 2.05 from statistical tables implies that there is a relationship among the independent variables and the regression equation is useful in predicting the magnitude of error in dif-

fusivities calculated from the initial slope method (Myers, 1989). The standard error for the model estimate is represented by variable S_{ey} . A significantly small value of S_{ey} shown in Table 5 is another indicator for the success of the regression equation. The variables in the last two rows of Table 5 are the regression sum of squares, SS_{Reg} , and the residual sum of squares, SS_{Res} , which indicate the variation due to regression line and the variation around the regression line, respectively. It is desired to achieve a large SS_{Reg} value in comparison to SS_{Res} value and this condition is satisfied for the fitted model shown in Eq. (14). The perfect fit of the empirical expression to the simulation data is shown in Fig. 1 where the % relative errors in diffusivity calculated from Eq. (9) is plotted against those predicted from Eq. (14). The result shown in Fig. 1 is not generally indicative of how the regression model will predict indeed, it is just a measure of quality of fit. In order to evaluate the predictive ability of Eq. (14), additional 75 simulations were performed for the combination of variables listed in Table 6. The parity plot of data generated from the simulations and calculated from the regression equation is shown in Fig. 2. The slope of the line in Fig. 2 determined as 0.9956 implies that Eq. (14) has both perfect correlative and predictive abilities within the range of variables considered. The effects of specific volumes of the solvent (\hat{V}_1) and the polymer (\hat{V}_2) as well as the step size ($\Delta\omega_{1E}$) on the % relative error in diffusivity computed from the initial slope method are shown in Figs. 3–5. For the case of constant \hat{V}_1 in Figs. 3a–d, the error in diffusivity decreases when the specific volume of the polymer increases; however, the magnitude of the decrease in error becomes smaller as both the step size, and the specific volume of the penetrant increase. For the case of constant \hat{V}_2 shown in Figs. 4a–d, the error increases as \hat{V}_1 increases but the effect of \hat{V}_1 on the increase of the error becomes less substantial at moderate and high values of the step size. In addition, at moderate and large step sizes, the magnitude of increase in error becomes larger as \hat{V}_2 increases. For the case of constant step size shown in Figs. 5a–d, the magnitude of error depends on the sign of $\Delta\hat{V} = \hat{V}_2 - \hat{V}_1$. As the difference between the specific volume of the polymer and the penetrant increases, the error in diffusivity becomes smaller for $\Delta\hat{V} > 0$ and larger for $\Delta\hat{V} < 0$. Finally, the maximum error in diffusivity is obtained at the largest step size when the difference in specific volumes of the penetrant and the polymer is maximum.

6. Conclusion

In this work, an empirical expression which is useful to predict the magnitude of error in diffusivity associated with the use of the traditional initial slope method was derived. The expression has both good correlative and predictive abilities. The simulation results indicated that not only the step size but also the difference between the specific volume of the penetrant and the polymer influences the magnitude of

error in diffusivities determined from typical differential sorption uptake curves. It is not meaningful to carry out a direct comparison between experimental differential sorption results with theoretical predictions if polymer film swells significantly due to large step size applied. Consequently, from practical point of view, the simple empirical expression derived here should serve as a useful guide in determining the appropriate step size during the differential-sorption experiment so that the magnitude of error in diffusivity associated with the use of the initial slope method is small.

Notation

D	binary diffusion coefficient
F	a ratio that expresses variance explained by the model divided by variance due to model error or experimental error
IS	the dimensionless initial slope of uptake curves presented as M_t/M_∞ as a function of $\sqrt{t^*}$
j_1^0	mass diffusion flux of solvent relative to velocity of polymer
L	initial thickness of the polymer film
M_t	mass of the penetrant per unit area that has entered a polymer film at time t
M_∞	mass of the penetrant per unit area that has entered a polymer film when equilibrium is reached
q_1	concentration variable
q_{1E}	equilibrium concentration
q_{10}	initial concentration
R^2	the coefficient of determination
SS_{Reg}	the regression sum of squares
SS_{Res}	the residual sum of squares
SS	sum of squared deviation of a factor
SS_T	the total sum of squared deviation
S_{ey}	the standard error for the model estimate
t	time
t^*	dimensionless time defined as $t^* = Dt/L^2$
v_1	species velocity of the solvent
v_2	species velocity of the polymer
\hat{V}_1	specific volume of pure solvent
\hat{V}_2	specific volume of pure polymer
x	distance variable in the direction of diffusion

Greek letters

$\Delta\hat{V}$	difference between the specific volume of the polymer and the penetrant
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$\Delta\omega_{1E}$	the difference between the equilibrium and initial concentration of the solvent
ξ	length variable
ξ_L	quantity defined as $\xi_L = \rho_{20}\hat{V}_2^0 L$
ρ_1	mass density of solvent in the film
ρ_2	mass density of polymer in the film
ρ_{20}	initial mass density of the polymer
ω^2	an index defined as the ratio of the sum of squared deviation of a factor (SS) to the total sum of squared deviation (SS_T)
ω_{1E}	equilibrium weight fraction of the solvent

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