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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.

Keywords: Absorption; Diffusion; Mass transfer; Polymer; Simulation; Swelling

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

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

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

are converted to the following equation:

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

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 $\xi(x,t) = \int_0^x \rho_2 \hat{V}_2 \, \mathrm{d}x$. If diffusive flux is expressed in terms of the new length and concentration variables,

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

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

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

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:

$$\left(\frac{\partial q_1}{\partial \xi}\right)_{\xi=0} = 0, \quad q_1(\xi_L, t) = q_{1E}, \quad q_1(\xi, 0) = q_{10},$$
$$\xi_L = \rho_{20} \hat{V}_2 L. \tag{6}$$

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)

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

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

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

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