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Solvent sorption in a polymer–solvent system – Importance of swelling and heat effects

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Abstract

Sorption experiments are often conducted in gravimetric sorption columns where several deviations from ideal conditions could potentially occur. For example, heat effects due to solvent sorption, errors introduced due to concentration dependent diffusion coefficients and swelling are unavoidable. In this study, we develop a model to study the importance of the combination of these effects in obtaining diffusion coefficients from sorption experiments. The model is used to explore a wide range of operating conditions and physical parameters.
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1. Introduction

The gravimetric sorption technique is a commonly used procedure to measure the mutual binary diffusion coefficient in polymer–solvent systems [1]. In this technique, the polymer film is placed in an evacuated glass column and exposed to a constant activity of pure solvent vapor. The solvent uptake is recorded as a function of time using a sensitive quartz spring. The polymer film can either be freely suspended (two-sided diffusion) or cast on a substrate (one-sided diffusion). From the raw data of solvent mass uptake versus time (sorption curve), the mutual binary diffusion coefficient is obtained using the initial slope method [2]. The initial slope method used to analyze raw data neglects swelling, assumes isothermal conditions, an instantaneous pressure change in the column and concentration independent diffusion behavior. The sorption curve obtained using the above assumptions is

referred to as the Fickian curve. However, during uptake experiments conducted in gravimetric sorption columns, one must consider the factors that could complicate the determination of diffusion coefficients. These include: (1) heat effects due to solvent absorption, (2) time lag for solvent activity to reach the desired value in the column, (3) swelling of the polymer film and (4) concentration dependent diffusion coefficient. Typical sorption experiments are made in small activity increments, which tend to decrease heat effects, minimize polymer swelling and limit changes in diffusion coefficient due to concentration. In addition, experimental conditions are selected to maintain the time scales associated with diffusion largely relative to the time required for the solvent to reach the desired activity in the column, thereby minimizing the effect of the non-instantaneous boundary condition change. However, it may not always be practical to choose experimental conditions to alleviate these effects.

A previous study has investigated and proposed a procedure to correct concentration effects [3], while other studies have addressed the effect of swelling [2,4]. Heat effects have been investigated in previous studies [5–8], and some of these studies have concentrated on investigating heat effects during sorption

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of solvents into zeolites [5,6]. Sorption into a macroporous system, such as a zeolite, is different from sorption into a typical polymeric film mainly because diffusion in the gas phase is unimportant in polymeric films considered in this study. The gas phase resistance is generally eliminated in a sorption experiment by having an essentially pure gas phase.

In a previous study, the effect of heat of sorption was investigated using water–wool and water–ethyl cellulose systems [9,10]. In more recent studies, heat effects were found to be important for the toluene–natural rubber system [11] and also for sorption studies conducted using the urethane/urea/ether block copolymer–dimethylacetamide system [7]. A relatively simple model was used in these studies to account for heat effects and heat transfer was approximated to occur through radiation. Further, the model involved a linear approximation to determine solubility change with temperature. Another study has been conducted to assess these effects [8], and the results of this study indicate that heat effects are extremely important during sorption in polymer–solvent systems. Further, they concluded that sigmoidal uptake curves commonly result from heat effects alone in typical gravimetric experiments.

The temperature rise during sorption can affect both the diffusivity and solubility in polymer–solvent systems. An increase in temperature increases the diffusivity but reduces activity of the solvent at the polymer–gas interface. The smaller activity of the solvent at the polymer–gas interface changes the boundary condition for solvent solubility at the interface. Thus, the effect of increasing temperature is a balance of two opposing factors. In this paper, we model these effects which can lead to difficulty and error in the estimation of the diffusion coefficient, and further systematically study the effects of these factors as a function of the dimensionless groups that result from the analysis. Our analysis does not invoke some of the linear approximations of previous studies, since our solutions are obtained numerically.

2. Model

Solvent sorption studies are often conducted in gravimetric sorption columns [1], and the progress of the experiment is followed by recording the weight gain of the polymer film as a function of time. While precautions are taken to maintain the column at a constant temperature, heat effects during solvent sorption into a polymer film cannot be avoided. Depending on the conditions of sorption, a significant change could occur between the measured and actual diffusion coefficients. Further, the moving boundary effects due to swelling of the film and the strong concentration dependence of diffusion coefficients for polymer–solvent systems are other complications involved in the analysis of differential sorption experiments. In this work, we develop a model to describe solvent sorption with coupled swelling and heat effects into a polymer film. The assumptions employed in describing this process are tabulated below.

1. The heat and mass transfer processes are considered to be one dimensional, since the length of the polymer film is large compared to the thickness.

2. The rate of heat transfer is much faster than the rate of mass transfer in the polymer film and the resistance to heat transfer lies predominantly in the gas phase. Consequently, the entire polymer film is assumed to be at a uniform temperature [12–14].
3. The diffusion coefficient is considered to be a function of concentration and temperature.
4. Heat transfer from the surface of the film is assumed to occur by a combination of convective transport and radiative transport. While radiative transport may not be significant at low temperatures, it may become important at high temperatures.
5. The temperature in the column is assumed to be constant.
6. Since the polymer film is at a uniform temperature, an overall energy balance is utilized to describe the change of the film temperature as a function of time.
7. The partial specific volume of each component is considered to be constant.
8. The problem is formulated in volume averaged coordinates. Consequently, while the polymer and solvent may have different partial specific volumes, a convection term does not arise in the analysis due to assumption 7.
9. The gas phase is treated as ideal to obtain the solvent activity from the knowledge of solvent partial pressures and solvent saturation pressures.
10. Solvent solubility in the polymer film is assumed to be adequately described using the Flory–Huggins theory.
11. The gas phase partial pressure is maintained at a constant value. Consequently, the activity change occurs only due to a change in the film temperature.
12. The physical properties such as density of the polymer and solvent, specific heats of the polymer, substrate and solvent and thermal conductivity are considered to be constants in the temperature range of interest.
13. Sorption is conducted at a temperature that is above the glass transition temperature of the pure polymer.
14. Instantaneous equilibrium is established at the surface of the polymer film.

Based on the assumptions described in the previous section, and ideas from precursor studies on diffusion in polymer–solvent systems, a model is formulated [12–14].

Utilizing assumptions 1, 3, 7, 8 and 13, the species continuity equation for the solvent in the polymer is given by:

$$\frac{\partial \rho_s}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial \rho_s}{\partial x}\right) \qquad (1)$$

Here, ρ_s denotes the concentration of the solvent in the polymer film, and D is the mutual binary diffusion coefficient.

The initial composition of the solvent in the polymer phase is assumed to be uniform.

$$\rho_s(t=0,x) = \rho_s^0 \qquad (2)$$

A no-flux boundary condition is imposed at the substrate–polymer interface since it is assumed that the substrate does not absorb any solvent. The second boundary (at the

polymer–gas interface) results from knowing the solvent activity at the polymer–gas interface and polymer–solvent interaction parameter. The boundary conditions are given below:

$$\frac{\partial \rho_s}{\partial x} = 0 \qquad \text{at } x = 0 \tag{3}$$

$$\ln(a) = \ln\left(\frac{P_{1g}}{P_{sat}}\right) = \ln \varphi_1 + \varphi_2 + \chi\varphi_2^2 \qquad \text{at } x = X(t) \tag{4}$$

In the above equations, $X(t)$ is the position of the polymer–gas interface and ρ_s^0 is the initial concentration of the solvent in the film, a is the solvent activity at the interface, φ_1 is the solvent volume fraction and φ_2 is the polymer volume fraction. Eq. (4) was derived based on assumptions 9, 10 and 11. Simply, the gas phase is treated as ideal and utilizing assumption 14, the partial pressure of the solvent in the gas phase, P_{1g}, becomes equal to equilibrium partial pressure of the solvent at the surface of the film. The knowledge of the activity and polymer–solvent interaction parameter yields solubility of the solvent in the polymer through the application of a thermodynamic theory. In this study, we use the Flory–Huggins theory to obtain solvent solubility from solvent activity. Eq. (4) assumes that the solvent activity changes due to a change in the saturation pressure, P_{sat}, which occurs as a result of heat evolved upon solvent absorption. Sorption data for most polymer–solvent systems are correlated well with a single Flory–Huggins interaction parameter, χ, which is usually found to be independent of temperature and concentration [15–18]. Therefore, we have considered a constant Flory–Huggins interaction parameter in our simulations.

In a volume averaged coordinate system,

$$(j_p^v)\hat{V}_p + (j_s^v)\hat{V}_s = 0 \tag{5}$$

In the above equation, j_p^v and j_s^v are the polymer and solvent fluxes in volume average coordinates, and $\hat{V}_s$ and $\hat{V}_p$ are the partial specific volumes of the solvent and polymer, respectively. While the initial thickness of the film is L, as solvent is absorbed, the gas–polymer interface moves. The movement of this boundary is given by Eq. (6), which is obtained from a polymer jump mass balance in conjunction with Eq. (5) and is recognized that the sum of the volume fraction of the polymer and solvent equals 1.

$$\frac{dX(t)}{dt} = \frac{D\hat{V}_s}{1 - \rho_s\hat{V}_s}\frac{\partial \rho_s}{\partial x} \tag{6}$$

$$X(t = 0) = L \tag{7}$$

The initial temperature in the film is assumed to be uniform

$$T(t = 0) = T_0 \tag{8}$$

Utilizing assumptions 2, 4, 5, 6 and 12, the time dependence of temperature change in the film is obtained as follows:

$$\frac{dT}{dt} =$$
$$\frac{\Delta H_{lv}\rho_p\frac{dX(t)}{dt} - h(T - T_0)|_{X(t)} - \sigma(T^4 - T_0^4)|_{X(t)} - h(T - T_0)|_{-H_1} - \sigma(T^4 - T_0^4)|_{-H_1}}{X(t)\rho_p\hat{c}_p^{poly} + H_1\rho_s^{subs}\hat{c}_p^{subs}} \tag{9}$$

ΔH_{lv} and h are the latent heat of vaporization of the solvent, the heat transfer coefficient of the gas phase on the polymer–substrate interface and polymer–gas interface. $\hat{c}_p^{poly}$ and $\hat{c}_p^{subs}$ are the heat capacities of the polymer and substrate, respectively. T is the temperature of the polymer and substrate, and H_1 is the thickness of the substrate and σ is the Stefan–Boltzmann constant. A thick substrate is essentially a heat sink and can be used to reduce the temperature rise in the film. In formulating the expressions for radiative heat transfer, it is assumed that the view factors are equal to 1.

Equations can be put into dimensionless form utilizing the following dimensionless variables.

$$\rho_s^* = \frac{\rho_s - \rho_s^0}{\rho_{eq} - \rho_s^0} \tag{10}$$

$$T^* = \frac{T}{T_0} \tag{11}$$

$$t^* = \frac{D_s^0 t}{L^2} \tag{12}$$

$$X^* = \frac{X}{L} \tag{13}$$

In these equations, D_s^0 is the initial mutual binary diffusion coefficient of the solvent in the polymer, L is the initial thickness of the film and ρ_{eq} is the equilibrium concentration of the solvent in the film. To immobilize the boundary, the coordinate transformation given below is used.

$$\xi = \frac{x}{X(t)} \tag{14}$$

Using the above dimensionless variables and the coordinate transformation, new form of the mass transfer equation in the polymer phase and the boundary conditions are given below.

$$\frac{\partial \rho_s^*}{\partial t^*} - \frac{\xi}{X^*}\frac{dX^*}{dt^*}\frac{\partial \rho_s^*}{\partial \xi} = \frac{1}{X^{*2}}\frac{\partial}{\partial \xi}\left(\frac{D}{D_s^0}\frac{\partial \rho_s^*}{\partial \xi}\right) \tag{15}$$

$$\frac{\partial \rho_s^*}{\partial \xi} = 0 \qquad \text{at } \xi = 0 \tag{16}$$

$$\ln(a) = \ln\left(\frac{P_{1g}}{P_{sat}}\right) = \ln \varphi_1 + \varphi_2 + \chi\varphi_2^2 \qquad \text{at } \xi = 1 \tag{17}$$

The initial condition becomes,

$$\rho_s^{0*}(t = 0, \xi) = 1 \tag{18}$$

The movement of the boundary is given by,

$$X^* \frac{dX^*}{dt} = G \frac{D}{D_s^0} \frac{\partial \rho_s^*}{\partial \xi}\bigg|_{\xi=1} \qquad (19)$$

The energy balance equation becomes,

$$\frac{dT^*}{dt^*} = \frac{B \dfrac{dX^*}{dt} - 2C(T^* - 1) - 2E(T^{*4} - 1)}{X^* + F} \qquad (20)$$

The dimensionless groups arising from the analysis are:

$$B = \frac{\Delta H_{lv}}{T_0 \hat{c}_p^p} \qquad (21)$$

$$C = \frac{hL}{D_s^0 \rho_p \hat{c}_p^p} \qquad (22)$$

$$E = \frac{\sigma L T_0^3}{D_s^0 \rho_p \hat{c}_p^p} \qquad (23)$$

$$F = \frac{H_1 \rho_s \hat{c}_p^{subs}}{L \rho_p \hat{c}_p^p} \qquad (24)$$

$$G = \frac{(\rho_{eq} - \rho_s^0) \hat{V}_s}{(1 - \rho_{eq} \hat{V}_s)} \qquad (25)$$

Dimensionless group B characterizes heat generation in the polymer film, while the groups C and E represent heat loss associated with convective transport and radiative transport, respectively. Group F represents the amount of heat absorbed by polymer film and substrate. An increase in the value of B and decrease in the values of C, E or F will raise the temperature of the polymer film, thereby amplifying the importance of heat effects. Conversely, decreasing the value of B and increasing the values of C, E or F will diminish the importance of heat effects. In typical gravimetric sorption columns, it is often difficult to estimate the heat transfer coefficients. However, the lowest value we can expect for the heat transfer coefficient is realized through radiation alone. Since we are in general talking of small temperature changes, we invoke the approximation $(T^{*4} - 1) = (T^* - 1)$. This further simplifies our expression given in Eq. (20) to

$$\frac{dT^*}{dt^*} = \frac{B \dfrac{dX^*}{dt} - \overline{D}(T^* - 1)}{X^* + F} \qquad (26)$$

The group $\overline{D} = 2C + 8E$ quantifies heat dissipation, and the lowest value for this term is realized when heat transfer occurs through radiation alone (i.e., $C = 0$). Further, if we are looking at a case where diffusion occurs through two sides of a plane sheet of thickness L, we can solve the same problem that has been formulated in this section by setting the dimensionless group $F = 0$ and changing the thickness of the film to $L/2$.

3. Results and discussion

The model equations represented by Eqs. (15) through (25) are non-linear partial and ordinary differential equations that are coupled. The equations were first converted into a set of non-linear algebraic equations using an implicit finite difference scheme. As in previous studies, the resulting equations were solved using the IMSL subroutine DNEQNF. In order to facilitate the numerical solution, a variable grid was used so that a finer finite difference grid spacing was imposed near the interface where steep concentration gradients occur [13,14]. The accuracy of the numerical solution was checked by increasing the number of grid points. For a differential step-change sorption experiment, sorption uptake or fractional approach to equilibrium is defined as $(M_t - M_i)/(M_\infty - M_i)$ where M_t is the mass of the penetrant in the polymer at any time, M_∞ is the final equilibrium mass uptake and M_i is the initial solvent mass in the polymer phase. In the following sections, error associated with neglecting swelling and heat effects was shown by presenting the results in terms of a ratio of the mass uptakes M_2/M_1 or M_1/M_0 which are defined below.

- M_0 is the sorption uptake calculated from the well-known analytical solution [19]. It should be rephrased that, in this solution, both swelling and heat effects are neglected and diffusion coefficient is assumed to be constant.
- M_1 is the sorption uptake calculated from the solution of Eqs. (15) through (25) which includes only the swelling effect.
- M_2 is the sorption uptake calculated from the solution of Eqs. (15) through (25) which includes both the moving boundary and heat effects.

In the calculation of sorption curves represented by M_1 and M_2, the diffusivity is considered as concentration and temperature dependent and is obtained from knowledge of the self-diffusion coefficient and thermodynamics of the polymer–solvent system [13,14]. The concentration and temperature dependence of the self-diffusion coefficient are obtained using the Vrentas–Duda free-volume theory [20,21] with appropriate free-volume parameters to determine the diffusion coefficient. In this study, a system having characteristics similar to the PVAC–toluene is used. The free-volume parameters are listed

Table 1
Parameters used to predict diffusivity as a function of temperature and concentration for all cases considered

Parameter	Value
D_0 (cm^2/s)	0.00825
E (J/mol)	7787.4
K_{11}/γ (cm^3/g K)	0.00157
K_{12}/γ (cm^3/g K)	0.000433
$K_{21}-T_{g1}$ (K)	−90.5
$K_{22}-T_{g2}$ (K)	−256
$\hat{V}_1^*$ (cm^3/g)	0.917
$\hat{V}_2^*$ (cm^3/g)	0.728
ζ	0.77
χ	0.5

in Table 1. In all simulations, sorption of the solvent through a freely suspended film was considered.

3.1. Effect of activity step

This section considers cases where activity step is varied at a constant column temperature. The parameters which are fixed for all simulations are given in Table 2. The influence of swelling on the sorption process is illustrated in Fig. 1a through c. As expected, predictions in these figures indicate that (1) the swelling effect becomes more significant for the larger step changes in solvent concentration; (2) at the beginning of the sorption, diffusivity of the solvent increases with an increase in the free volume of the polymer. When the rate of increase in diffusivity is larger than the rate of increase in swelling, deviation from the analytical solution increases with time and shows a maxima. During the later stages of sorption, the influence of the rate of increase in swelling becomes larger than the diffusional resistance and the rate of sorption decreases resulting in a decline in the ratio of M_1/M_0. All curves approach to a value of 1, i.e., analytical and numerical solutions converge, as sorption proceeds toward equilibrium. Fig. 1b and c indicates that the effect of swelling depends not only on the magnitude of jump in activity but also is a function of the activity at the beginning of the sorption process. The influence of heat effect on the mass uptake process is shown in Fig. 2a through c. Predictions in these figures clearly indicate that heat of sorption has a greater significance at higher solvent activity levels compared to lower solvent activity levels and its contribution on the overall sorption process increases with increasing activity step. We have utilized the predicted uptake curves to estimate the magnitude of error that would occur if one simply uses traditional initial slope method. For this purpose, diffusivity obtained from the slope of the initial linear portion of the predicted uptake curves, D_p, was compared with that obtained from the analytical solution, D_a, and the absolute error in the diffusivity was defined as follows:

$$\text{\%Absolute error in diffusivity} = \left| \left| \ln D_a \right| - \left| \ln D_p \right| \right| \times 100.$$

As illustrated in Fig. 3a through c, the errors in diffusivity due to the swelling and heat effect increase with increasing activity step and the contribution of heat effect is more pronounced at high activity levels. This can be explained by larger rate of swelling at higher activity levels, which in turn leads to a higher temperature rise in the film.

3.2. Effect of column temperature

Gravimetric sorption experiments are usually carried out at different column temperatures in order to determine diffusivities as a function of temperature. To investigate the individual
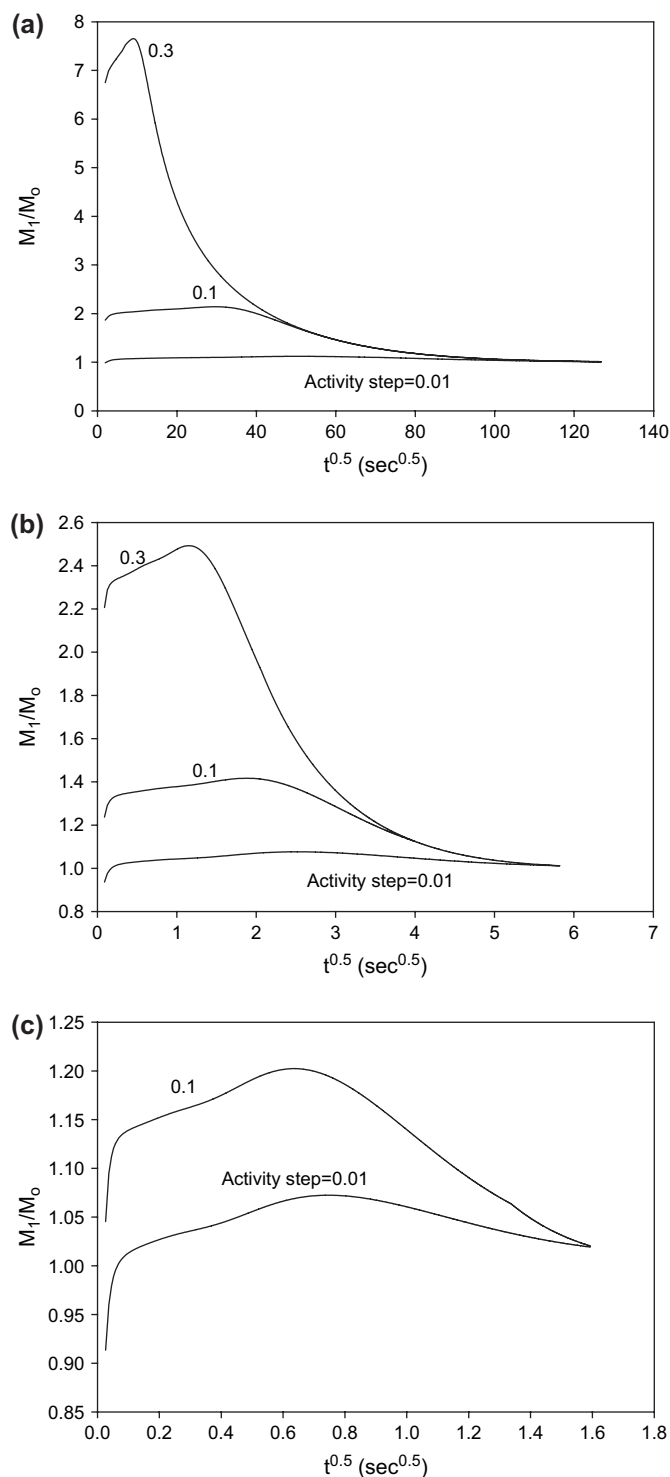

Fig. 1. Effect of swelling on sorption uptake. Initial activity level in the column is (a) zero, (b) 0.4 and (c) 0.7, initial temperature in the film is 340 K and the latent heat of vaporization of the solvent is 290 J/g. The numbers on each curve represent the activity step applied.

Table 2
Input parameters which are fixed for all simulations

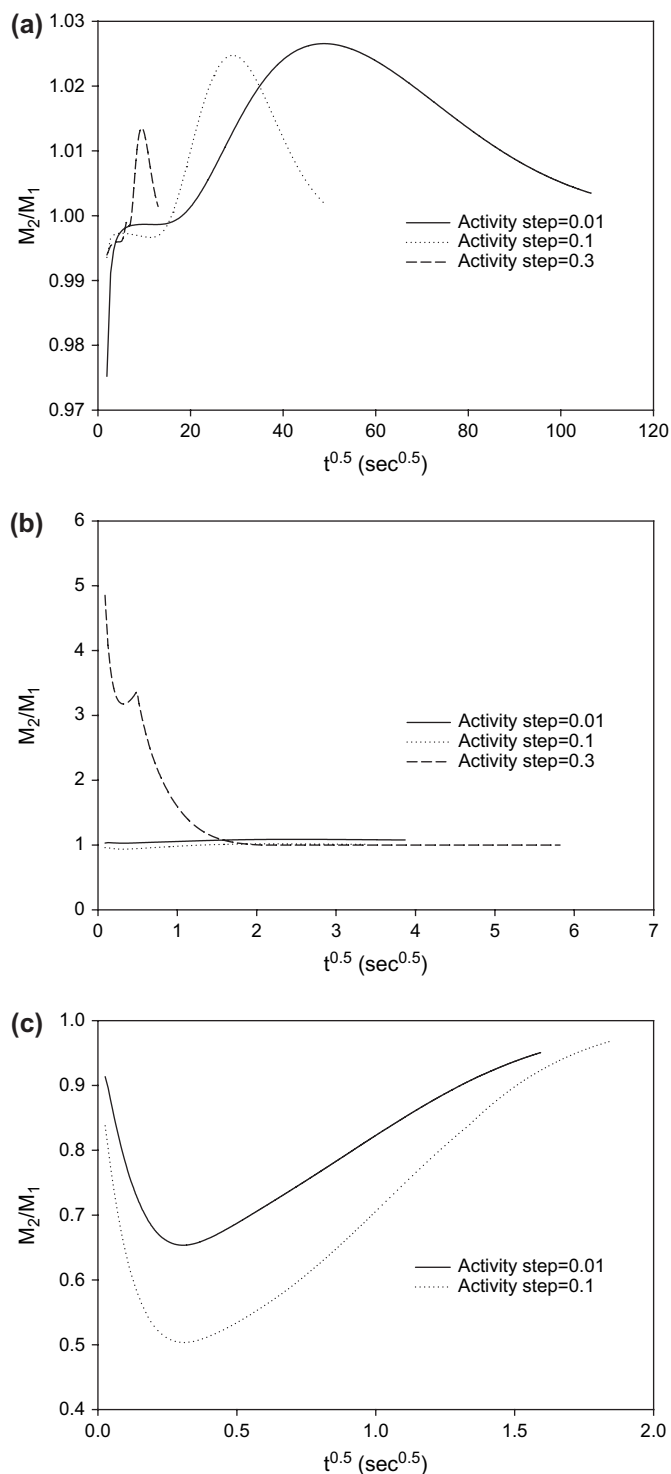| Parameter	Value
Initial thickness of the film (μm)	10
Specific volume of the solvent (cm^3/g)	1.15
Specific volume of the polymer (cm^3/g)	0.85
Specific heat of the polymer film (J/g K)	1.65
Density of the polymer film (g/cm^3)	1.18
Heat transfer coefficient (W/cm^2 K)	0.011

Fig. 2. Contribution of heat of effect on sorption uptake as a function of activity step applied. Initial activity level in the column is (a) zero, (b) 0.4 and (c) 0.7, initial temperature in the film is 340 K and the latent heat of vaporization of the solvent is 290 J/g.
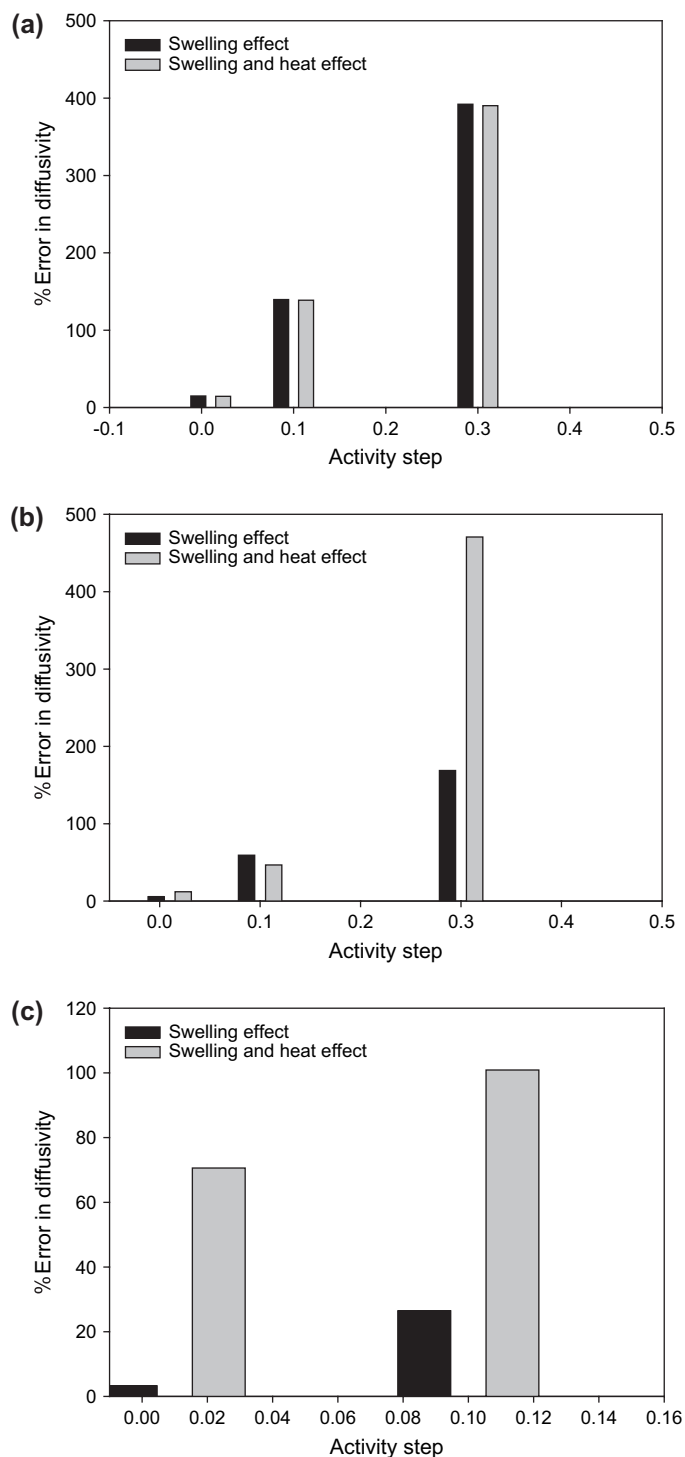
Fig. 3. % Error in estimating the diffusivities from the initial slope method as a function of the activity step applied. Initial activity level in the column is (a) zero, (b) 0.4 and (c) 0.7, initial temperature in the film is 340 K and the latent heat of vaporization of the solvent is 290 J/g.

contributions of the swelling and heat effects on the overall sorption process at different column temperatures, uptake curves were determined for cases corresponding to column temperatures ranging from 340 K to 400 K. In these predictions, the initial concentration of the solvent in the film was zero, and the activity step was maintained constant at 0.1. As column temperature is raised, the rate of increase in film thickness becomes larger than the rate of increase in diffusivity, thus, the sorption of the solvent into the film becomes slower. Consequently, the deviation of the sorption curve
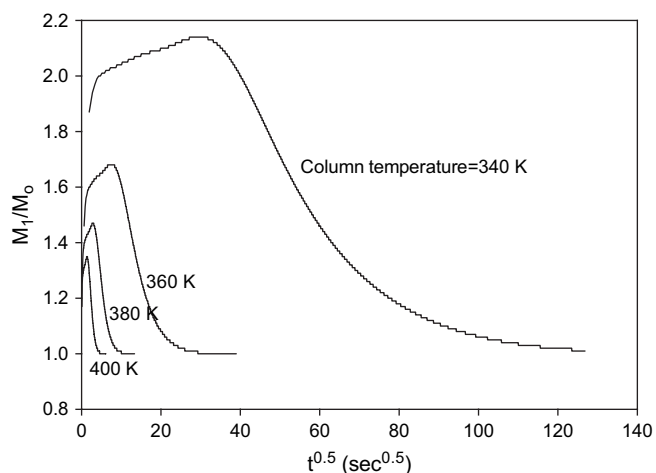
Fig. 4. Effect of swelling on sorption uptake as a function of the initial temperature in the film. Initial activity level in the column is zero, activity step is 0.1 and the latent heat of vaporization of the solvent is 290 J/g.
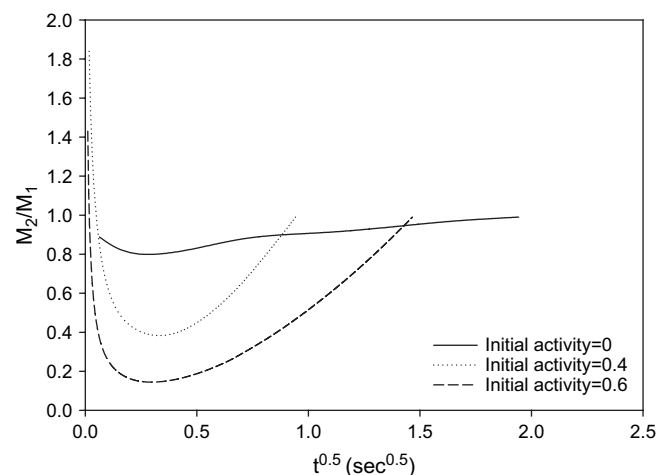

Fig. 6. Contribution of heat of effect on sorption uptake as a function of the initial activity level in the column. Initial temperature in the film is 400 K, activity step is 0.3 and the latent heat of vaporization of the solvent is 2500 J/g.

from the analytical curve due to the swelling decreases with increasing column temperature as shown in Fig. 4. Compared to the swelling effect, the contribution of the heat effect was not found to change significantly with the column temperature. Fig. 5 shows that errors in diffusivities associated with neglecting the heat effect are insignificant and it decreases with increasing column temperature. However, as shown in Fig. 6 the influence of heat effect on the overall sorption process becomes significant when the high column temperature and high solvent activity in the column are coupled with a large activity step and a large heat of vaporization of the solvent. This result can be explained by higher temperature rise in the film due to larger rate of swelling of the film and larger heat of vaporization of the solvent. Fig. 7 shows that the errors in diffusivities are mainly due to the heat effect at high activity

levels in the column. In certain cases, the errors in diffusivities associated with swelling are larger than that when both swelling and heat effect are considered as shown in Figs. 3b and 7. These predictions imply that the rate of sorption becomes slower due to significant temperature rise in the film. This is observed when the mutual diffusion coefficient decreases with increasing solvent concentration, i.e., when the thermodynamic forces dominate the mutual diffusion process. The competing effects of increasing free volume and thermodynamic interactions cause a maximum in the mutual diffusion coefficient as a function of solvent concentration. The maximum shifts to lower solvent concentrations as temperature in the film increases. In this case, both the swelling and diffusion processes serve to increase the rate of mass transfer resistance in the film.
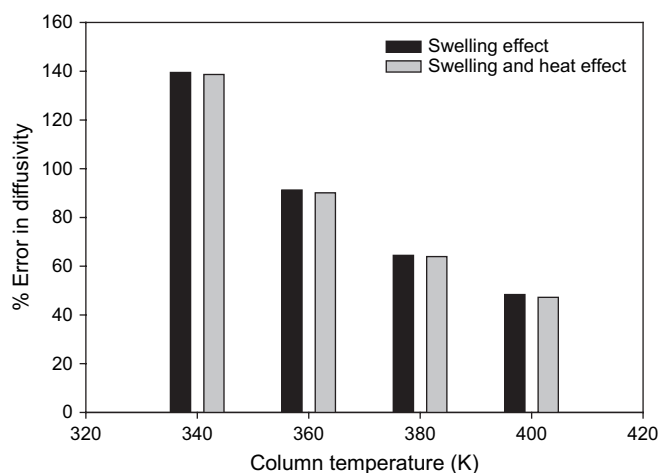

Fig. 5. % Error in estimating the diffusivities from the initial slope method as a function of the initial temperature in the film. Initial activity level in the column is zero, activity step is 0.1 and the latent heat of vaporization of the solvent is 290 J/g.
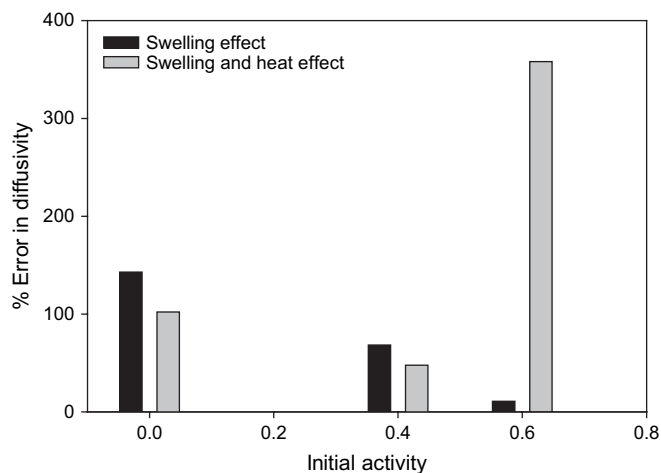

Fig. 7. % Error in estimating the diffusivities from the initial slope method as a function of the initial activity level in the column. Initial temperature in the film is 400 K, activity step is 0.3 and the latent heat of vaporization of the solvent is 2500 J/g.
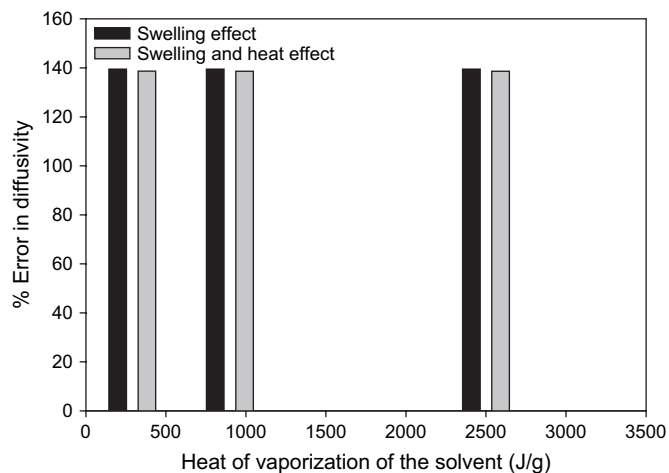
Fig. 8. % Error in estimating the diffusivities from the initial slope method as a function of the latent heat of vaporization of the solvent. Initial temperature in the film is 340 K, initial activity level in the column is zero and activity step is 0.1.

3.3. Effect of heat of vaporization

We have predicted the uptake curves and calculated the magnitude of error in diffusivities for different heat of vaporization values. Fig. 8 shows that when initial activity level and temperature in the column are zero and 340 K and a moderate activity step of 0.1 is applied, then the magnitude of error in diffusivities does not change with the heat of vaporization of the solvent. However, at higher column temperatures and when larger activity step is applied, then, heat of vaporization of the solvent becomes an important parameter in determining the contribution of the heat of sorption. With increased heat of vaporization and larger activity step applied, both the value of the dimensionless group, B, and rate of swelling in Eq. (26) become larger causing a rise in the temperature of the film, thereby amplifying the importance of heat effect.

4. Conclusion

In this study, we have developed a model to assess the importance of the swelling and heat effects on the overall sorption process. We have analyzed our simulation results like we would treat experimental data to determine the magnitude of errors that would result if these effects are neglected. The results have shown that not only the step size but also the activity at the beginning of the sorption process determine the magnitude of error in diffusivities due to both swelling and heat effects. The complex nature of polymer—solvent thermodynamics and the exponential nature of the saturation pressure temperature relationship do not allow for a simple criterion to determine the importance of heat effects. However, we have shown that heat effect becomes significant when both the activity level and the temperature in the column are high and the large step size is applied. Under these conditions, the latent heat of vaporization of the solvent also makes an important contribution on the heat effect. The predictions imply that in order to minimize the error in diffusivities associated with the use of initial slope method, it is necessary to apply smaller step sizes at high activity levels and column temperatures.

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