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Short Communication

ISOTHERMAL DRYING RATE OF ETHYLBENZENE FROM A SPHERICAL POLYSTYRENE PELLET

Jin San Yoon

Department of Polymer Science and Engineering, Inha University, Incheon 402-751, Korea

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Abstract—Desorption behaviour of ethylbenzene from a spherical polystyrene pellet was investigated. The predicted drying rate using an average diffusion coefficient differed substantially from that simulated with concentration dependent diffusivity. As the drying temperature decreased and the initial solute content of the pellet increased, the difference between the two calculations became more significant.

Key words: *Desorption, Simulation, Ethylbenzene, Polystyrene*

INTRODUCTION

Polymers leaving polymerization processes usually contain volatile substances such as unreacted monomers, solvents or reaction regulators. Removal of the volatile residuals has recently experienced considerable interest to meet enviornmental and health regulations. The design of dryers to remove the volatiles from the polymer pellets requires informations on the binary diffusivity for the volatile solute/polymer system. The diffusion coefficient for the solute/polymer system depends strongly on solute concentration as well as on temperature. The free volume theory predicts this complex diffusional behaviour reasonably well [Liu, 1980].

In the present study, the drying rate of ethylbenzene from a spherical polystyrene pellet was simulated by integrating the unsteady state diffusion equation by means of the numerical method proposed by Patankar. The parameters were those from the free volume theory for the ethylbenzene/polystyrene system reported by Duda et al. in 1982.

DESCRIPTION OF THE MODEL

1. The Free Volume Theory

The free volume theory for diffusion of solute in polymer matrix has been derived by Duda and Berens as:

$$D_1=D_{O1}\ \exp\left\{-\frac{w_1\hat{V}_1^*+(1-w_1)\hat{V}_2^*\xi}{w_1(K_{11}/\gamma)(K_{21}+T-T_{g1})+(1-w)(K_{12}/\gamma)(K_{22}+T-T_{g2})}\right\}(1-2\chi\phi_1)(1-\phi_1)^2 \quad (1)$$

where ϕ_1, w_1 and T are the solute volume fraction, the weight fraction and the desorption temperature respectively. All the other parameters of Eq. (1) from free volume theory are determined experimentally from viscosity and density data of the solute and the polymer as a function of temperature, solubility of the solute, diffusivity at some solute concentrations, and so on. Symbols and notations are the same as appeared in the original paper.

The values of the parameters for ethylbenzene/polystyrene system are tabulated in Table 1. These parameters are valid at temperatures well above the glass transition temperature of polystyrene.

2. Diffusion Equation

The following diffusion equation describes the variation of solute concentration in a spherical pellet:

$$\frac{\partial C}{\partial t}=\frac{1}{r^2}\frac{\partial}{\partial r}\left(Dr^2\frac{\partial C}{\partial r}\right) \quad (2)$$

$$t=0 \quad C=C_o \quad (3)$$

$$r=0 \quad \frac{\partial C}{\partial r}=0 \quad (4)$$

$$r=R \quad -D\frac{\partial C}{\partial r}\bigg|_{r=R}=k\left(C_{r=R}-C_{eq}\right) \quad (5)$$

where R is the pellet radius and C_{eq} is the equilibrium solubility of the solute. The mass transfer coefficient k for a single sphere in a stagnant fluid can be estimated as

$$Sh=2.0 \quad (6)$$

where Sh, the Sherwood number is defined as kd_p/D_b. Other types of correlations for the mass transfer coefficient are well documented by Floyd. The diffusion coefficient, D_b, for the binary mixture of air and ethylbenzene vapor can be estimated as described in Perry's Chemical Engineers' Handbook:

$$D_b=\frac{10^{-3}T^{1.75}\left(\frac{1}{M_{air}}-\frac{1}{M_{EB}}\right)^{1/2}}{P\{(\Sigma v)_{air}^{1/3}+(\Sigma v)_{EB}^{1/3}\}} \quad (7)$$

Table 1. Parameters of the free volume theory for ethylbenzene/polystyrene system [Duda et al., 1982].

Parameter	$\hat{V}_1^*$ cm^3/g	$\hat{V}_2^*$ cm^3/g	K_{11}/γ cm^3/g·K	K_{12}/γ cm^3/g·K	K_{21}-T_g K	K_{22}-T_g K	χ	ξ	D_o cm^2/s
Data	0.946	0.850	2.05×10^{-3}	5.82×10^{-4}	−96.7	−327	0.45	0.56	6.92

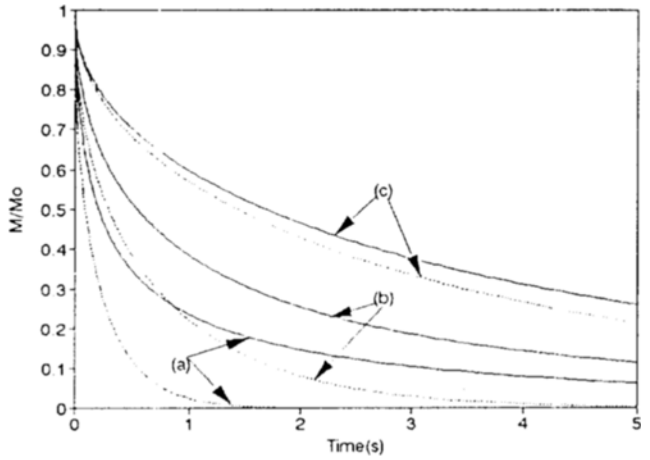

Fig. 1. The nondimensionalized quantity of ethylbenzene in a polystyrene pellet at different initial solute concentrations. Partial pressure of the solute in the drying gas phase was set to be zero.
(a) $C_o=0.1$ (b) $C_o=0.05$ (c) $C_o=0.01$ (g/g of polymer)
Solid line : Variable diffusion coefficient
Dotted line : Constant average diffusion coefficient
Temperature : 140℃
Pellet radius : 0.2 cm

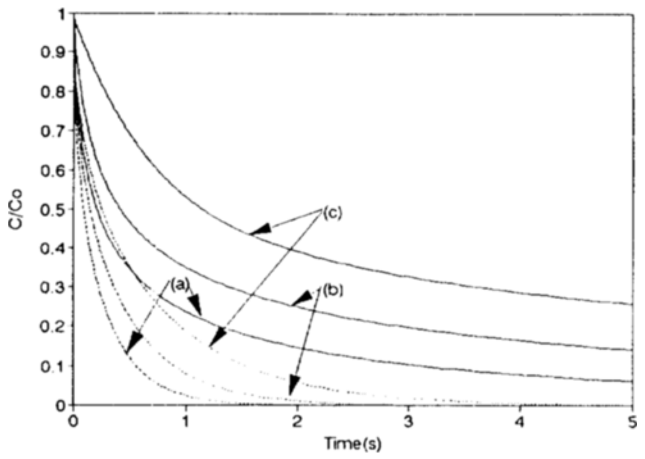

Fig. 2. Effect of desorption temperature on residual ethylbenzene quantity in a spherical polystyrene pellet.
(a) 140℃ (b) 130℃ (c) 120℃
Solid line : Variable diffusion coefficient
Dotted line : Constant average diffusion coefficient.
Initial solute concentration $C_o=0.1$ (g/g of polymer)
Pellet radius : 0.2 cm

$(\Sigma v)_{air}$ was set to be 20.1 and $(\Sigma v)_{EB}$ was calculated to be 131.6 from the values of the atomic diffusion volumes. P, T, M_{air} and M_{EB} are the pressure, temperature and molar mass of air and ethylbenzene respectively.

For constant diffusion coefficient, the analytical solution of Eq. (2) can be found in Crank's book as

$$\frac{C-C_{eq}}{C_o-C_{eq}}=\frac{2LR}{r}\sum_{n=1}^{\infty}\frac{\exp(-D\beta_n^2t/R^2)}{\{\beta_n^2+L(L-1)\}}\frac{\sin(\beta_n/R)}{\sin(\beta_n)} \tag{8}$$

where $L=Rk/D$ and the β_n's are the roots of

$$\beta_n \cot \beta_n+L-1=0$$

When the diffusivity is dependent on the solute concentration, numerical method is of great practical use.

Nondimensionalization of the diffusion Eq. (2) gives

$$\frac{\partial\zeta}{\partial\theta}=\frac{1}{\eta^2}\frac{\partial}{\partial\eta}\left(\frac{D}{\overline{D}}\eta^2\frac{\partial\zeta}{\partial\eta}\right) \tag{9}$$

where $\zeta=C/C_o$, $\theta=\overline{D}t/R$ and $\eta=r/R$. Eq. (9) is linearized to integrate numerically as described briefly in the appendix.

CALCULATION RESULTS AND DISCUSSION

The present numerical integration scheme predicted the solute concentration profile exactly identical to that obtained from the analytical solution (8) assuming constant diffusivity. This implies that the numerical method is suitable to integrate Eq. (9).

In Fig. 1, solid line shows the amount of residual solute in the pellet as a function of drying time. Dotted lines correspond to the desorption behaviour predicted with average constant diffusivity estimated by

$$D_{av}=\frac{\int_0^{c_o} D\,dC}{C_o} \tag{10}$$

where D is given as a function of solute concentration as in Eq. (1).

It can be seen from Fig. 1 that the rate of decrease of the dimensionless solute quantity (M/M_o) becomes faster as the initial solute concentration of the pellet is increased. This is because the diffusion coefficient becomes higher with an increase in the initial concentration of the solute.

At initial stage of drying, the solute concentration in the polymer pellet is high. Hence the diffusivity obtained from Eq. (1) would be larger than the constant average diffusivity given by Eq. (10). As a result, when the constant average diffusivity was used instead of the concentration dependent diffusivity, it was expected that the solute would be simulated to diffuse out more slowly at an early stage of the drying and then the situation would be reversed later in time. However, as shown in Fig. 1, the rate of the solute desorption predicted with the constant average diffusivity was always faster than that calculated with the concentration dependent diffusivity from the beginning without any reversion.

This can be explained as follows: The solute concentration of the outer shell layer in contact with gas phase reaches almost the equilibrium value from the outset of the drying, and the variable diffusivity at this layer would assume a quite low value corresponding to the diffusivity at the solute concentration in equilibrium with the gas phase solute content. Eq. (11) calculates an average diffusivity for mass transfer between i^{th} and $(i-1)^{th}$ shell layer using the two diffusivities estimated by Eq. (1) with the respective solute concentration in each shell [Patanka, 1980]

$$D_{av}=\frac{2}{1/D_i+1/D_{i-1}} \tag{11}$$

Note that D_{av} would be zero if either D_i or D_{i-1} is zero. This has physical meaning since mass transfer rate would become zero in this case.

The effect of temperature on the desorption rate is shown in Fig. 2. Higher drying temperatures desorb the solute faster than lower drying temperatures. As previously shown in Fig. 1, the amount of residual solute simulated with the constant average diffusivity decreases always faster than that calculated with the concentration dependent diffusivity. However the difference between calculations using either constant average diffusivity or concerntration dependent diffusivity is smaller as desorption temperature increases and/or as initial solute concentration decreases.

In summary, we concluded that the drying rate calculated with constant average diffusivity would be quite erroneous particularly when the initial solute concentration is high or when the desorption temperature is low.

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APPENDIX

The discretization equation for the numerical integration of Eq. (9) is derived by multiplying η^2 on each side and integrating it over a small control volume and over a time interval from θ to $\theta+\Delta\theta$:

$$\int_{\theta}^{\theta+\Delta\theta}\int_{m}^{n}\eta^2\frac{\partial\zeta}{\partial\theta}d\eta\ d\theta=\int_{\theta}^{\theta+\Delta\theta}\int_{m}^{n}\frac{\partial}{\partial\eta}\left(\frac{D}{\overline{D}}\eta^2\frac{\partial\zeta}{\partial\eta}\right)d\eta\ d\theta \tag{A1}$$

For i^{th} shell, it can be linearized as

$$(\zeta_i-\zeta_i^o)\frac{1}{3}(\eta_n^3-\eta_m^3)=\int_{\theta}^{\theta+\Delta\theta}\left[\frac{D_n}{\overline{D}}\eta_n^2\left(\frac{\zeta_{i+1}-\zeta_i}{\Delta\eta_n}\right)\right.$$
$$\left.-\frac{D_m}{\overline{D}}\eta_m^2\left(\frac{\zeta_i-\zeta_{i-1}}{\Delta\eta_m}\right)\right]d\theta \tag{A2}$$

where ζ_{i+1}, ζ_i, and ζ_{i-1} are dimensionless solute concentrations at i+1, i and i−1th shells, respectively. ζ_i^o is the old value of ζ_i. A fully implicit scheme adopts values of the ζ's at $\theta+\Delta\theta$, and Eq. (A2) reduces to:

$$a_i\zeta_i=a_{i+1}\zeta_{i+1}+a_{i-1}\zeta_{i-1}+a_i^o\zeta_i^o \tag{A3}$$

where $a_{i+1}=\frac{D_n}{\overline{D}}\eta_n^2\frac{1}{\Delta\eta_n}$

$$a_{i-1}=\frac{D_m}{\overline{D}}\eta_m^2\frac{1}{\Delta\eta_m}$$
$$a_i^o=\frac{1}{3}\frac{\eta_n^3-\eta_m^3}{\Delta\eta}$$
$$a_i=a_{i+1}+a_{i-1}+a_i^o$$

D_n and D_m are average diffusion coefficients determined by Eq. (11) with the diffusivities corresponding to the solute concentration at i+1 and i, i and i−1 shell respectively. The diffusion coefficients were interatively recalculated with the new value of the solute concentration at each shell until a sufficient convergence is attained.

At the center of the pellet Eq. (A3) becomes

$$a_o\zeta_o=a_1\zeta_1+a_o^o\zeta_o^o \tag{A4}$$

with

$$a_1=\frac{D_n}{\overline{D}}\eta_n^2\frac{1}{\Delta\eta_n}$$
$$a_o^o=\frac{\eta_n^3}{3\Delta\theta}$$
$$a_o=a_1+a_o^o$$

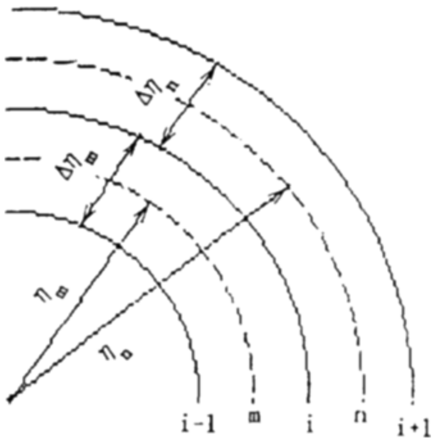

Fig. A1. Discretization of the spherical pellet.

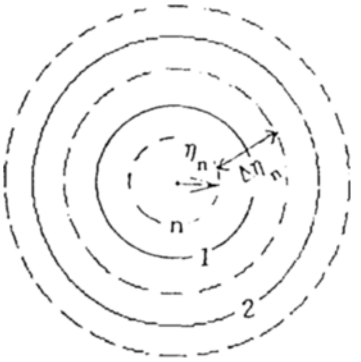

Fig. A2. Discretization around the center of the pellet.

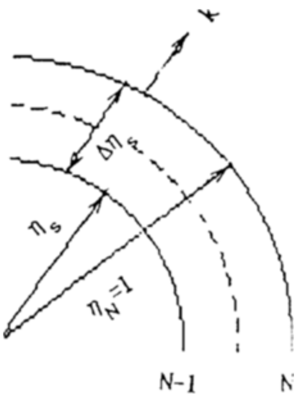

Fig. A3. Discretization around the surface of the pellet.

Eq. (A3) and (A4) constitutes n equations with (n+1) unknowns. The needed one additional equation can be gotten from the material balance around the surface of the pellet.

$$\zeta_N=\frac{\frac{D_s}{\Delta\eta_s}\frac{\eta_s^2}{}\zeta_{N-1}+kR\frac{C_{eq}}{C_0}+\frac{1}{3}(1-\eta_s^3)\frac{\overline{D}}{\Delta\theta}\zeta_N^o}{kR+\frac{D_s\ \eta_s^2}{\Delta\eta_s}+\frac{1}{3}(1-\eta_s^3)\frac{\overline{D}}{\Delta\theta}} \tag{A5}$$

Where k is mass transfer coefficient and R is the pellet radius. The Tri Diagonal-Matrix Algorithm described by Patankar solves easily the (n+1) equations without excessive computing time.

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