Prediction of Polymer/Solvent Diffusion Coefficients Using Free-Volume Theory

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자유부피이론을 이용한 고분자/용매 확산계수의 예측

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1. Introduction

Molecular diffusion of small molecules in polymers plays an important role in many areas where polymers are acting as barriers, and in separation processes, such as selective diffusion. Different applications of polymers have different requirements on their transport properties. Therefore, reliable predictions of diffusion coefficients for small molecules in polymeric materials could be a useful tool to design appropriate materials. For many years, the theories based on free-volume concepts have been widely used to correlate and predict diffusion behavior in polymer/solvent systems. In the theory derived by Vrentas and Duda,[1] the empty space between molecules that is available for molecular transport, referred to as hole free-volume, is being redistributed. Molecular transport will occur only when a free-volume of sufficient size appears adjacent to a molecule and the molecule has enough energy to jump into this void. The diffusive jump is considered complete when the void left behind is closed before the molecule returns to its original position. In this paper, the Vrentas-Duda free-volume theory is presented and the methods to estimate free-volume parameters for predicting polymer/ solvent diffusion coefficients are described in detail.

2. Vrentas-Duda Free-Volume theory

According to the Vrentas-Duda free-volume theory for diffusion, the solvent self-diffusion coefficient, D_1, and the polymer/solvent binary mutual diffusion coefficient, D, are expressed by[1]

$$D_1 = D_0 \exp\left(\frac{-E}{RT}\right) \exp\left(\frac{-(\omega_1 \hat{V}_1^* + \xi \omega_2 \hat{V}_2^*)}{\omega_1(\frac{K_{11}}{\gamma})(K_{21} - T_{g_1} + T) + \omega_2(\frac{K_{12}}{\gamma})(K_{22} - T_{g_2} + T)}\right)$$

$$D = D_1(1 - \phi_1)^2(1 - 2\chi\phi_1)$$

Here, D_0 is a pre-exponential facor, E is the critical energy which a molecule must possess to overcome the attractive forces holding it to its neighbors, and γ is an overlap factor which is introduced because the same free- volume is available to more than one molecule. $\hat{V}_i^*$ is the specific hole free- volume of component I required for a jump, w_i is the weight fraction of component I, and ξ is the ratio of the molar volume of the jumping unit of the solvent to that of the polymer. K_{11} and K_{21} are free-volume parameters for the solvent, while K_{12} and K_{22} are those for the polymer, φ_1 is the solvent volume fraction, and χ is the polymer/solvent interaction parameter. Although there are 13 independent parameters in the equation, grouping some of them means that 10 parameters ultimately need to be evaluated; K_{11}/γ, $K_{21}-T_{g1}$, K_{12}/γ, $K_{22}-T_{g2}$, $\hat{V}_1^*$, $\hat{V}_2^*$, χ, D_0, E, and ξ. In order to predict polymer/solvent diffusion coefficients, all parameters need to be determined without using any diffusivity data. Methods for estimating free-volume parameters to predict diffusion behavior are discussed in the following section.

3. Estimation of Free-Volume Parameters

(1) The two critical volumes, $\hat{V}_1^*$ and $\hat{V}_2^*$, can be estimated as the specific volumes of the solvent and polymer at 0 K. Molar volumes of the solvent and polymer at 0 K can be estimated using group contribution methods summarized by Haward.[2]

(2) The parameters K_{12}/γ and $K_{22}-T_{g2}$ are simply related to the WLF constants of the polymer, C_{12} and C_{22}, as follows:[3]

$$\frac{K_{12}}{\gamma} = \frac{\hat{V}_2^*}{2.303 C_{12} C_{22}}$$

$$K_{22} - T_{g2} = C_{22} - T_{g2}$$

(3) The parameters K_{11}/γ and $K_{21}-T_{g1}$ can be estimated using one of the

following equations:[4,5]

$$\ln \eta_1 = \ln A_1 + \frac{(\gamma \widehat{V}_1^* / K_{11})}{(K_{21} - T_{g1}) + T}$$

$$\ln \tau_c = \ln A_1' + \frac{(\gamma \widehat{V}_1^* / K_{11})}{(K_{21} - T_{g1}) + T}$$

where η_1 and τ_c are solvent viscosity and correlation time, respectively.

(4) In addition, D_o and E can be estimated by combining the Dullien equation for the self-diffusion coefficient of pure solvents[6] with the Vrentas-Duda free-volume equation evaluated in the limit of pure solvents as follows

$$\ln \left(\frac{0.124 \times 10^{-16} \widehat{V}_c^{2/3} RT}{\eta_1 M_1 \widehat{V}_1} \right) = \ln D_o - \frac{E(\omega_1 \rightarrow 1)}{RT} - \frac{\gamma \widehat{V}_1^* / K_{11}}{K_{21} - T_{g1} + T}$$

Here, $\widehat{V}_c$ (cm^3/mol) and M_1 (g/mol) are the solvent's critical molar volume and molecular weight, respectively.

(5) For a solvent molecule which moves as a single unit, the parameter ξ may be defined as

$$\xi = \widehat{V}_1^{\,o}(0) \,/\, \widehat{V}_{2j}^*$$

where $\widehat{V}_1^{\,o}(0)$ and $\widehat{V}_{2j}^*$ are the solvent molar volume at 0 K and the molar volume of the polymer jumping unit, respectively. If it is assumed that the size of the polymer jumping unit is independent of the solvent, $\widehat{V}_{2j}^*$ can be determined from the ξ versus $\widehat{V}_1^{\,o}(0)$ plot. Once $\widehat{V}_{2j}^*$ is known for a particular polymer, the value of ξ for any solvent in that polymer can be determined as far as the solvent moves as a single unit. If an $\widehat{V}_{2j}^*$ value is not available for a certain polymer, it can be estimated using the following correlation:[7]

$$\widehat{V}_{2j}^* \;(cm^3/mol) = 0.0925\, T_{g2}(K) + 69.47 \qquad (T_{g2} < 295\ K)$$
$$= 0.6224\, T_{g2}(K) - 86.95 \qquad (T_{g2} \geq 295\ K)$$

(6) Finally, the Flory-Huggins polymer/solvent interaction parameter, χ, can be determined from the solubility data where the equilibrium volume fraction of the solvent in the polymer is known as a function of solvent vapor pressure, P_1:

$$P_1/P_1^o = \phi_1 \exp(\phi_2 + \chi\phi_2^2)$$

where P_1^o is the solvent saturation vapor pressure.

4. References

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