Determination of Free-Volume Parameters from Diffusivity Data in Glassy Polymers

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INTRODUCTION

The free-volume theory of transport has proved to be a useful vehicle for describing molecular motion in concentrated polymer-solvent systems. This theory can be used to provide satisfactory predictions and correlations of the temperature and concentration dependences of mutual and self-diffusion coefficients above the glass transition temperature of the system.[1-3] It has further been proposed that free-volume theory should provide a satisfactory description of the diffusion of trace amounts of solvents in amorphous, glassy polymers.[4,5] Furthermore, free-volume theory has been used to estimate the effects of temperature and concentration on the viscosity of concentrated polymer solutions above the glass transition temperature of the system.[6] Finally, the temperature variations of the viscosity of a pure liquid below its glass transition temperature have also been described using the free-volume theory of transport.[7]

Free-volume theory is based on the hypothesis that only part of the volume of a material, the hole free volume, is available for molecular transport. Hence, although the parameters of the theory have a definite physical interpretation, some of them cannot be measured directly since they involve properties of the hole free volume, which is a somewhat vaguely defined quantity. Consequently, transport data are utilized to determine these free-volume parameters. For example, rheological data above the glass transition temperature of a polymer can be used to compute the WLF (Williams-Landel-Ferry) constants for the polymer and hence to produce two equations for three of the parameters of the free-volume formulation.[8] Clearly, the three polymer free-volume parameters cannot be determined individually from this procedure unless an additional assumption is introduced or additional data are available.

Plazek and Magill[7] have illustrated a method of determining these three free-volume parameters for an organic liquid by using rheological data taken both above and below the glass transition temperature of the liquid. Fillers and Tschoegl[9] suggested that the parameters of free-volume theory could be determined unambiguously by combining isobaric measurements of mechanical polymer properties at atmospheric pressure as a function of temperature with isothermal measurements as a function of pressure. In this paper, we present a method of determining the three free-volume parameters for an amorphous polymer from diffusivity data for a trace amount of a solvent in the polymer collected at temperatures below the polymer glass transition temperature. The theoretical basis of the method is discussed in the second

Journal of Applied Polymer Science, Vol. 33, 2581–2586 (1987)
CCC 0021-8995/87/072581-06$04.00

section of the paper, and results for three polymers are presented in the third section.

THEORY

The basis of the theoretical discussion in this paper is the hypothesis that the diffusion of a trace amount of solvent in the polymer can be described by the free-volume theory of transport both above and below the glass transition temperature of the pure polymer.[4,5] In the limit of zero penetrant concentration, the temperature dependence of the mutual diffusion coefficient D at some temperature T can be described using an effective activation energy for diffusion E_D, which can be defined as

$$E_D = RT^2\left(\frac{\partial \ln D}{\partial T}\right)_p \tag{1}$$

It has been shown elsewhere[4] that the temperature variation of E_D below the polymer glass transition temperature T_{g2} is given by the expression

$$E_D = \frac{RT^2\left(\gamma \hat{V}_2^* \xi / \lambda K_{12}\right)}{\left[K_{22}/\lambda + \left(T - T_{g2}\right)\right]^2} \tag{2}$$

Here, γ is an overlap factor introduced because the same free volume is available to more than one molecule. Cohen and Turnbull[10] have suggested that γ should lie between $\frac{1}{2}$ and 1. The quantity $\hat{V}_2^*$ is the minimum local hole free volume per gram of polymer required for the displacement of a polymeric jumping unit, and ξ is the ratio of the critical molar volume of the solvent jumping unit to the critical molar volume of the polymer jumping unit.

The parameter λ, which describes the character of the change of the volume contraction that can be attributed to the glass transition, is defined as

$$\lambda = \frac{\alpha_{2g} - \left(1 - f_{H2}^G\right)\alpha_{c2}}{\alpha_2 - \left(1 - f_{H2}^G\right)\alpha_{c2}} \tag{3}$$

Here, α_2 is an average thermal expansion coefficient that describes the volumetric behavior of the equilibrium liquid above T_{g2}, and α_{2g} is an average thermal expansion coefficient for the glassy state that describes the temperature dependence of the volume of the nonequilibrium liquid below T_{g2}. Furthermore, α_{c2} is the thermal expansion coefficient of pure polymer for the sum of the specific occupied volume and the specific interstitial free volume (the volume not available for transport). Also, f_{H2}^G, the fractional hole free volume of the pure polymer at the glass temperature, is defined as

$$f_{H2}^G = \frac{\hat{V}_{FH2}\left(T_{g2}\right)}{\hat{V}_2^0\left(T_{g2}\right)} \tag{4}$$

where $\hat{V}_{FH2}(T_{g2})$ is the specific hole free volume of the polymer at T_{g2} and

$\hat{V}_2^0(T_{g2})$ is the specific volume of the pure polymer at the glass transition temperature. Finally, K_{12} and K_{22} are free-volume parameters for the polymer, which are defined as

$$K_{12} = \hat{V}_2^0(T_{g2})\left[\alpha_2 - \left(1 - f_{H2}^G\right)\alpha_{c2}\right] \tag{5}$$

$$K_{22} = \frac{f_{H2}^G}{\alpha_2 - \left(1 - f_{H2}^G\right)\alpha_{c2}} \tag{6}$$

As noted above, the three free-volume parameters for the polymer, γ, α_{c2}, and f_{H2}^G, have a definite physical interpretation, but they are not directly measurable quantities. However, it is possible to derive equations from which these parameters can be calculated using appropriate volumetric, rheological, and diffusion data. Since the parameters K_{12} and K_{22} are related to the WLF constants[8] for the polymer, $(C_1^g)_2$ and $(C_2^g)_2$, by the equations

$$\frac{\gamma \hat{V}_2^*}{K_{12}} = 2.303(C_1^g)_2(C_2^g)_2 \tag{7}$$

$$K_{22} = (C_2^g)_2 \tag{8}$$

it is easy to derive the following equations for γ, α_{c2}, and f_{H2}^G by using eqs. (3) and (5) through (8):

$$f_{H2}^G = (C_2^g)_2 \frac{\alpha_2 - \alpha_{2g}}{1 - \lambda} \tag{9}$$

$$\alpha_{c2} = \frac{\alpha_{2g} - \lambda\alpha_2}{(1 - \lambda)\left(1 - f_{H2}^G\right)} \tag{10}$$

$$\gamma = \frac{2.303(C_1^g)_2\hat{V}_2^0(T_{g2})f_{H2}^G}{\hat{V}_2^0(0)} \tag{11}$$

In the derivation of these equations, it has been assumed that $\hat{V}_2^*$ is equal to the specific occupied volume of the polymer, which is defined as $\hat{V}_2^0(0)$, the equilibrium specific volume of the liquid polymer at 0 K.

The parameters α_{2g}, α_2, and $\hat{V}_2^0(T_{g2})$ are generally available from volumetric data for the polymer, and the quantity $\hat{V}_2^0(0)$ can be estimated using methods discussed by Haward.[11] The WLF constants $(C_1^g)_2$ and $(C_2^g)_2$ can be determined using rheological data, and these parameters have been tabulated for a large number of polymers.[8] Consequently, the parameters γ, α_{c2}, and f_{H2}^G can be computed from eqs. (9) through (11) if an estimate of λ is available. It is proposed here that this parameter be calculated from eq. (2) using diffusivity data for an appropriate solvent in the glassy polymer. The chosen solvent should be one that has the entire solvent molecule as a jumping unit. If D versus T data are available below T_{g2} for the diffusion of a trace amount of this solvent in the polymer, then eq. (1) can be used to determine E_D at some temperature, say T_1, below T_{g2}. Indeed, E_D values for diffusion in glassy polymers are available for penetrant diffusion in a number of polymers.[12] Hence, since K_{22} and $\gamma\hat{V}_2^*/K_{12}$ can be determined for a particular polymer from the WLF constants [using eqs. (7) and (8)] and since T_{g2} values are available for most polymers, eq. (2) can be used to determine λ from the measured value of E_D for the polymer-solvent system of interest if the parameter ξ is known for this polymer-solvent mixture.

The parameter ξ can be determined by one of two ways. Diffusivity versus temperature data for the same polymer-solvent system above T_{g2} can be used to determine ξ by a procedure discussed elsewhere.[13,14] Alternatively, diffusivity data above T_{g2} for other solvents in the same polymer can be used to estimate ξ for the polymer-solvent system for which diffusivity data are available below T_{g2}. It has been shown[13,15] that $\gamma\hat{V}_2^*\xi/K_{12}$ should be a linear function of the molar volume at 0 K of the jumping unit of the solvent. Consequently, a plot of $\gamma\hat{V}_2^*\xi/K_{12}$ versus the molar volume at 0 K of the entire solvent molecule should be a straight line through the origin for all solvents that jump as single units. Indeed, it has been shown[16,17] that an equation of the form

$$\frac{\gamma\hat{V}_2^*\xi}{K_{12}} = \bar{B}\tilde{V}_1^0(0) \tag{12}$$

provides a satisfactory representation of diffusivity data for penetrant diffusion in five amorphous polymers. Here, $\tilde{V}_1^0(0)$ is the molar volume of the equilibrium liquid solvent at 0 K; this can be estimated using methods discussed by Haward.[11] The constant $\bar{B}$ has been tabulated for four amorphous polymers.[16] Consequently, eq. (2) can be rewritten as

$$E_D(T_1) = \frac{RT_1^2\lambda\bar{B}\tilde{V}_1^0(0)}{\left[K_{22} + \lambda(T_1 - T_{g2})\right]^2} \tag{13}$$

so λ can be easily determined if a value of E_D is available at some temperature T_1 for solvent diffusion in the glassy polymer and if $\bar{B}$ has been evaluated for the polymer under consideration.

An example of the calculation of λ from eq. (13) using E_D data for glassy polymers is illustrated in Table I for penetrant diffusion in polystyrene. Values of λ are calculated from E_D data for six penetrants[12,18,19] using eq. (13), with $\bar{B}$ = 10.5 K g mol/cm^3 for polystyrene.[16] It is evident from this

TABLE I
Calculation of λ from Penetrant Diffusion Data in Polystyrene

Penetrant	Temperature (°C)	E_D (kcal/g mol)	λ	Reference
Hydrogen	25	4.0	0.15	12
Oxygen	25	8.3	0.23	
Carbon dioxide	25	8.7	0.20	
Neon	25	4.4	0.20	18
Argon	25	7.8	0.21	
Methane	30	9.3	0.20	19

TABLE II
Free-Volume Parameters for Amorphous Polymers

Polymer	λ	f_{H2}^{G}	$\alpha_{c2} \times 10^{4}$ (K^{-1})	γ
Polystyrene	0.20	0.025	0.31	0.90
Poly(vinyl acetate)	0.18	0.026	1.6	1.1
Poly(methyl methacrylate)	0.35	0.044	0.59	1.6

table that, with the exception of the λ value calculated using hydrogen diffusion data, there is generally good agreement among the calculated values of λ. In this paper, the free-volume parameters of the polymer are identified as γ, α_{c2}, and f_{H2}^{G}, whereas the three polymer free-volume constants are often denoted as B, α_f, and f_g in the literature.[8] The relationships between these two sets of parameters are given by the following equations:

$$f_g = f_{H2}^{G} \tag{14}$$

$$\alpha_f = \alpha_2 - \left(1 - f_{H2}^{G}\right)\alpha_{c2} \tag{15}$$

$$B = \frac{\gamma \hat{V}_2^{*}}{\hat{V}_2^{0}\left(T_{g2}\right)} \tag{16}$$

RESULTS AND DISCUSSION

The three free-volume parameters for three amorphous polymers were calculated from eqs. (9) through (11) using representative literature values[4,6,8,11] for α_{2g}, α_2, $\hat{V}_2^{0}(T_{g2})$, $\hat{V}_2^{0}(0)$, $(C_1^{g})_2$, $(C_2^{g})_2$, and λ. It would of course be preferable if all these physical properties were available for the same polymer sample, but it does not appear that all these parameters have been reported for a single sample of a particular polymer. The results of these calculations are presented in Table II. The three values for f_{H2}^{G} appear to be reasonable, and in fact, the f_{H2}^{G} values for two of the polymers are essentially identical to the "universal" value of 0.025.[8] The calculated values for α_{c2} are in all three cases significantly less than α_{2g}. In two of the three cases, α_{c2} is less than 25% of the estimated value of α_{2g}. These results appear to be consistent with the expansion coefficient results reported by Plazek and Magill[7] and Fillers and Tschoegl.[9] Consequently, all the available evidence points to the conclusion that $\alpha_{c2} \approx 0$ is generally a better approximation than $\alpha_{c2} \approx \alpha_{2g}$, although it is clear that α_{c2} is generally not identically equal to zero. Finally, two of the three values of γ fall outside the range suggested by Cohen and Turnbull.[10] However, there is evidence that this suggested range is not strictly valid. Ricci et al.[20] analyzed computer experiments for hard spheres and concluded that the computer calculations supported the exponential dependence on free volume suggested by the Cohen-Turnbull theory. However, for the special case of hard spheres, they estimated that $\gamma = 1.69$.

This work was supported by National Science Foundation Grant CPE-8207401 and by funds provided by the Dow Chemical Company.

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Received March 24, 1986
Accepted August 11, 1986