Diffusion of Small Molecules in Amorphous Polymers

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ABSTRACT: A new version of the free volume theory of molecular transport is used to provide an explanation for the difference between the diffusional behavior of small molecules and of organic diluents in amorphous polymers. Equations are derived which illustrate the effect of solvent size or molecular weight on the concentration and temperature dependence of the mutual diffusion coefficient in polymer–solvent systems. It is concluded that the apparent failure of the free volume theory in describing the diffusion of small molecules in polymeric systems is really a failure of a limited form of the theory rather than of the theory itself.

Diffusion in concentrated polymer solutions is usually described by application of the free volume theory of molecular transport, and this theory has achieved some degree of success in describing the diffusional behavior of organic solvents in amorphous polymers.[2] However, the free volume theory of diffusion which has been formulated by Fujita[2] does not correctly predict the concentration dependence of the mutual diffusion coefficient for penetrant molecules of small size in amorphous polymers. For example, Fujita has noted the significant difference which exists between the diffusional behavior of water and of organic solvents in amorphous polymers in temperature intervals extending as high as about 60 °C above the glass transition temperature of the polymer. The mutual diffusion coefficient, D, for the poly(methyl acrylate)–ethyl acetate system exhibits a strong dependence on concentration[2] above the glass transition temperature, whereas the diffusion coefficients for the poly(methyl acrylate)–water[2] and poly(vinyl acetate)–water[3] systems show little or no concentration dependence. The viscoelastic measurements of Fujita and Kishimoto[4] show that water is more effective than a typical organic solvent such as methanol in increasing the free volume of both poly(methyl acrylate) and poly(vinyl acetate), and, hence, it was concluded by Kishimoto et al.[3] and by Fujita[2] that free volume theory could not describe the diffusion of small molecules, such as water, in amorphous polymers. Kishimoto et al.[3] also observed that diffusion coefficients for polymer–water systems are less temperature dependent than for polymer–organic solvent mixtures.

There is also some evidence that free volume theory does not describe the temperature dependence of the mutual diffusion coefficients for systems composed of a trace of small penetrant molecules in amorphous polymers. Meares[5,6] measured the diffusion coefficients of seven gases in poly(vinyl acetate) in a temperature interval of about 20 °C just above the glass transition temperature of the polymer. He concluded that plots of the logarithm of D vs. $1/T$ for these small penetrants were linear so that the activation energy for diffusion of each of these gases is independent of temperature. On the other hand, for the poly(methyl acrylate)–methanol system, Fujita et al.[7] observed a significant variation in the effective activation energy for diffusion of a trace of penetrant in a temperature interval of about 30 °C. Furthermore, free volume theory does not predict an Arrhenius relationship for the temperature dependence of the diffusion coefficient at zero solvent concentration at temperatures relatively close to the glass transition temperature of the polymer. From these observations, it would again appear that the Fujita version of the free volume theory does not describe the diffusional behavior of systems composed of small penetrants and amorphous polymers. However, it should be noted that Kishimoto et al.[3] observed a slight curvature in the logarithm of D vs. $1/T$ plot for the poly(methyl acrylate)–water system by considering a significantly larger temperature interval (50 °C) than that utilized by Meares.[5,6]

To explain the apparent failure of free volume theory for diffusion involving small molecules, Kishimoto et al.[3] speculated that diffusion in systems with small penetrants proceeds by a localized cooperation of the vibrations of a few monomer units on the polymer chain and, hence, is independent of the average free volume in the system. A similar point of view is taken by Frisch[8] who states that the minimum void volume needed for the movement of very small penetrant molecules is less than the average void volume of the system, and diffusion of these penetrants occurs by movement of the solvent molecules into preexisting cavities. Frisch et al.[9] extended this basic idea and derived a modified free volume theory valid for the diffusion of small molecules in polymers. It is not the purpose of the present paper to discuss the merits of these explanations or to comment on the validity of the modified free volume theory. However, it should be noted that calculations based on a new version of the free volume theory show[10,11] that the above explanations may not be entirely satisfactory. These calculations indicate that the free volume available for molecular transport (denoted as the hole free volume in the discussion below) in pure polystyrene is about 3.5% of the volume of the polymer at 150 °C, 50 °C above the glass transition temperature of undiluted polystyrene. Furthermore, the minimum free volume required for the displacement of a hydrogen molecule (as estimated using the molar volume of liquid hydrogen at 0 °K) is more than two times the average hole free volume associated with each polymeric jumping unit. The movement of a water molecule requires more than three times this average free volume. Hence, it would appear that a significant redistribution of the free volume in the system must take place even if molecules as small as hydrogen and water are to undergo movement through the polymer. The average hole free volume per polymeric jumping unit can, of course, be increased by raising the temperature of the system, but, at temperatures too far above the glass transition, the diffusion process is no longer dominated by free volume considerations and the energy needed to overcome attractive forces becomes important.

The purpose of this paper is to provide a possible explanation for the difference between the diffusional behavior of small molecules and of organic diluents in amorphous polymers. This is done by assuming that the diffusion of small amounts of solvent in a relatively wide temperature interval (perhaps of the order of 100 °C) just above the glass transition temperature of the polymer is a free volume dominated process for penetrants of all sizes. The analysis is based on a new version[10] of the free volume theory which is a more general adaptation of the theory of Cohen and Turnbull[12] to polymer–solvent diffusion than is the theory proposed by Fujita.[2] This modified free volume theory forms the basis of a proposed method[11] for the prediction of the concentration, temperature, and molecular weight dependence of diffusion coefficients in amorphous polymer–solvent systems. It is shown below that the temperature and concentration dependence of penetrants of all sizes can be predicted from the results of this theory, and the apparently anomalous diffusion results described above for small penetrants are readily explained within the framework of the theory. It is concluded that the apparent failure of the free volume theory in describing the diffusion of small molecules in polymeric systems is really a failure of a limited form of the theory rather than of the theory itself.

Generalization of the Free Volume Theory

From a generalization of the free volume theory of Cohen and Turnbull[12] for polymer–solvent diffusion, it can be shown[10] that the self-diffusion coefficient of the solvent, D_1, is given by the following expression:

$$D_1 = D_{01} \exp\left[-\frac{\gamma(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)}{\hat{V}_{FH}}\right] \tag{1}$$

Here, γ is an overlap factor (which should be between ½ and 1) which is introduced because the same free votume is available to more than one molecule, $\hat{V}_I^*$ is the specific critical hole free volume of component I required for displacement of this component, ω_I is the mass fraction of component I, $\hat{V}_{FH}$ is the average hole free volume per gram of mixture, and the subscripts 1 and 2 refer to solvent and polymer, respectively. Furthermore, the quantity ξ is defined by the equation

$$\xi = \tilde{V}_1^*/\tilde{V}_2^* = \hat{V}_1^* M_1/\hat{V}_2^* M_j \tag{2}$$

where $\tilde{V}_1^*$ is the critical volume of solvent per mole of solvent, $\tilde{V}_2^*$ is the critical volume of polymeric jumping units per mole of jumping units, M_1 is the molecular weight of the solvent, and M_j is the molecular weight of a jumping unit. The preexponential factor, D_{01}, is a much weaker function of temperature than the exponential term, and, hence, it can be treated as a constant.

It has been shown elsewhere[10] that eq 1 is a more general expression for D_1 than that proposed by Fujita,[2] and the further assumptions sufficient for the validity of the equation presented by Fujita are listed and discussed in detail. For the purpose of this investigation, the key assumption implicitly introduced by Fujita is that the molecular weight of the solvent is equal to the molecular weight of a jumping unit of the polymer chain:

$$M_1 = M_j \tag{3}$$

Clearly, eq 3 limits the applicability of Fujita's version of the free volume theory to a class of solvents with molecular weight not too different than M_j. For organic solvents, it can be expected that the molecular weight of the solvent is relatively close to that of the polymeric jumping unit since the polymer is often formed from a monomer which itself is an organic solvent. Hence, it is reasonable to expect that the diffusional behavior of such solvents can be explained by the theory of Fujita. On the other hand, for small molecules of low molecular weight, M_1 will be significantly less than M_j, and the predictions of the Fujita version of the free volume theory will no longer be acceptable. It is thus not surprising that the Fujita theory describes diffusion of ethyl acetate ($M_1 = 88$) in poly(methyl acrylate) but not diffusion of water ($M_1 = 18$) in the same polymer. A calculation based on the new version of the free volume theory,[10,11] using appropriate viscosity and diffusion data, indicates that M_j for polystyrene is 167, approximately 1.5 times the molecular weight of a typical organic solvent, such as ethylbenzene, for this polymer.

Equation 1 will serve as the starting point for investigating the effect of solvent size on the concentration and temperature dependence of D. The variation of the concentration dependence of D with the size of the solvent is examined by deriving an expression for the derivative of D with respect to the solvent mass density in the limit of zero solvent concentration. The effect of the size of the solvent on the temperature dependence of D can be ascertained by evaluating D at $\omega_1 = 0$ and constructing plots of the logarithm of D vs. $1/T$ for various solvent sizes.

Concentration Dependence of D

The concentration dependence of D for small concentrations of solvent can be represented by an equation of the form

$$D = D_0[1 + k_D \rho_1 + \cdots] \tag{4}$$

where D_0 is the mutual diffusion coefficient at zero solvent concentration and ρ_1 is the mass density of the solvent. Since the series coefficient k_D is obviously given by

$$k_D = \left[\left\{\frac{\partial(D/D_0)}{\partial \rho_1}\right\}_{T,p}\right]_{\rho_1=0} \tag{5}$$

evaluation of this quantity for a given temperature and pressure and for a particular polymer directly illustrates how the nature of the solvent affects the concentration dependence of D.

It has been shown elsewhere[10] using the formalism of Bearman[13] that D and D_1 are related by the equation

$$D = \frac{D_1 \rho_2 \hat{V}_2 \rho_1}{RT(1 - (D_1/D_1^*))}\left(\frac{\partial \mu_1}{\partial \rho_1}\right)_{T,p} \tag{6}$$

where ρ_2 is the mass density of the polymer, $\hat{V}_2$ is the partial specific volume of the polymer, and μ_1 is the chemical potential of the solvent per mole. Furthermore, D_1^* is defined by the equation

$$D_1^* = RTM_1/\rho_1 \zeta_{11} N_A^2 \tag{7}$$

where N_A is Avogadro's number and ζ_{11} is one of the friction coefficients introduced by Bearman.[13] By appropriate utilization of series expressions for the concentration-dependent quantities in eq 6, it can be shown that

$$k_D = 2A_2M_1 - a_1 - 2\hat{V}_{10} + F_1 + \frac{N_A^2 \zeta_{11}^0 D_1^0}{RTM_1} \tag{8}$$

The quantity A_2 is the second virial coefficient in the chemical potential relationship for the polymer

$$\mu_2 = \mu_2^0 - RT\tilde{V}_2^0 \rho_1 \left(\frac{1}{M_1} + A_2 \rho_1 + \cdots\right) \tag{9}$$

where μ_2 is the chemical potential per mole of polymer in the mixture, μ_2^0 is the chemical potential per mole of pure polymer, and $\tilde{V}_2^0$ is the molar volume of the pure polymer. Furthermore, $\hat{V}_{10}$ is the partial specific volume of the solvent in the limit of zero solvent concentration, ζ_{11}^0 and D_1^0 are values of the friction coefficient and self-diffusion coefficient at zero solvent concentration, and a_1 and F_1 are defined by the following series expansions:

$$D_1 = D_1^0[1 + F_1 \rho_1 + \cdots] \tag{10}$$

$$\hat{V}_2 = \hat{V}_2^0[1 + a_1 \rho_1 + \cdots] \tag{11}$$

Here, $\hat{V}_2^0$ is the specific volume of the pure polymer and $D_1^0 = D_0$.

For the evaluation of k_D, it is of course necessary to know the limiting value of the friction coefficient, ζ_{11}^0. Since free volume theory provides equations only for the self-diffusion coefficients of solvent and polymer, D_1 and D_2, it is not in general possible to deduce $\zeta_{11}{}^0$ from free volume considerations alone. An additional equation relating the friction coefficients is needed, but, at the present time, there appears to be no approximate theory which can be readily evaluated to produce such an expression for polymer–solvent systems. Furthermore, there are insufficient experimental data for mutual and self-diffusion coefficients which can be used to suggest the form of an equation relating these quantities for binary mixtures of polymeric and simple liquids. If the geometric mean relationship

$$\zeta_{12} = (\zeta_{11}\zeta_{22})^{1/2} \tag{12}$$

is assumed valid for the three friction coefficients, it can then be shown that

$$\frac{N_A{}^2\zeta_{11}{}^0 D_1{}^0}{RTM_1} = \frac{D_2{}^0 M_2 \hat{V}_2{}^0}{D_1{}^0 M_1} \tag{13}$$

where $D_2{}^0$ is the self-diffusion coefficient of the entire polymer molecule at zero solvent concentration and M_2 is the polymer molecular weight. Clearly, for this special case, the last term in eq 8 can be determined using only the equations of free volume theory for self-diffusion coefficients. For the polystyrene–ethylbenzene system, calculations for the temperature interval 100 to 200 °C and for M_2 ranging from 10^4 to 10^6 show that the maximum value of $N_A{}^2\zeta_{11}{}^0 D_1{}^0/RTM_1$ is 0.01 cm^3/g, and, hence, the last term in eq 8 is obviously small compared to the other terms. It is reasonable to expect that this conclusion will be valid for any amorphous polymer–solvent system in the vicinity of the glass transition temperature of the polymer. This conclusion is of course based on a specific form of the equation relating the friction coefficients, but the conclusion may still be valid even if the equation relating ζ_{11}, ζ_{12}, and ζ_{22} is significantly different than eq 12. Data are needed on the mutual and self-diffusion processes in polymer–solvent systems so that the nature of the expression relating ζ_{11}, ζ_{12}, and ζ_{22} can be deduced. For the time being, it seems reasonable to expect that the last term of eq 8 is not important, and, indeed, it can be easily shown that Fujita implicitly introduces an equivalent assumption into his analysis.

From eq 1, it is evident that

$$\left(\frac{\partial \ln D_1}{\partial \omega_1}\right)_{\omega_1=0} = \frac{\gamma\xi\hat{V}_2{}^*}{[\hat{V}_{FH}(0)]^2}\left(\frac{\partial \hat{V}_{FH}}{\partial \omega_1}\right)_{\omega_1=0} - \frac{\gamma\hat{V}_1{}^*}{\hat{V}_{FH}(0)} + \frac{\gamma\xi\hat{V}_2{}^*}{\hat{V}_{FH}(0)} \tag{14}$$

where $\hat{V}_{FH}(0)$ is the specific hole free volume at $\omega_1 = 0$. Upon introduction of eq 2, this result can also be written in the following form:

$$\left[\frac{\partial \ln (D_1/D_1{}^0)}{\partial \omega_1}\right]_{\omega_1=0} = \frac{\gamma\hat{V}_2{}^*\xi}{\hat{V}_{FH}(0)}\left[\frac{(\partial\hat{V}_{FH}/\partial\omega_1)_{\omega_1=0}}{\hat{V}_{FH}(0)} + 1 - \frac{M_j}{M_1}\right] \tag{15}$$

In the proposed free volume theory,[10] the volume of the material is divided into occupied volume, interstitial free volume, and hole free volume. The specific occupied volume of a pure liquid is defined to be the specific volume of the equilibrium liquid at 0 °K, and the specific interstitial free volume of a material is the unoccupied volume which is distributed uniformly among the molecules of a given species because the energy for redistribution of this volume is large. The specific hole free volume of a liquid is the volume associated with the discontinuous distribution of holes in the liquid, and it is assumed that this free volume can be redistributed with no increase in energy. The specific hole free volume for a binary mixture of solvent and polymer is thus given by

$$\hat{V}_{FH} = \hat{V} - \omega_1[\hat{V}_1{}^0(0) + \hat{V}_{FI1}(T_{G1})]\exp\left(\int_{T_{G1}}^{T}\alpha_{c1}\,dT\right) - \omega_2[\hat{V}_2{}^0(0) + \hat{V}_{FI2}(T_{G2})]\exp\left(\int_{T_{G2}}^{T}\alpha_{c2}\,dT\right) \tag{16}$$

where $\hat{V}$ is the specific volume of the binary mixture, $\hat{V}_I{}^0(0)$ is the specific volume of pure component I at 0 °K, T_{GI} is the glass transition temperature of component I, and $\hat{V}_{FI1}(T_{G1})$ and $\hat{V}_{FI2}(T_{G2})$ are the specific interstitial free volumes of solvent and polymer at their glass transition temperatures. In addition, α_{cI} is the thermal expansion coefficient for component I for the sum of the specific occupied volume and the specific interstitial free volume. Equation 16 is based on the assumption of additivity of the volumes formed from the sum of the specific occupied volume and the specific interstitial free volume. Differentiation of eq 16 and evaluation at $\omega_1 = 0$ give

$$\left(\frac{\partial\hat{V}_{FH}}{\partial\omega_1}\right)_{\omega_1=0} = \left(\frac{\partial\hat{V}}{\partial\omega_1}\right)_{\omega_1=0} + \hat{V}_{FH}(1) - \hat{V}_1{}^0 - \hat{V}_{FH}(0) + \hat{V}_2{}^0 \tag{17}$$

where $\hat{V}_{FH}(1)$ is the specific hole free volume at $\omega_1 = 1$ and $\hat{V}_1{}^0$ is the specific volume of pure solvent. In general,

$$(\partial\hat{V}/\partial\omega_1)_{T,p} = \hat{V}_1 - \hat{V}_2 \tag{18}$$

where $\hat{V}_I$ is the partial specific volume of component I, and, hence, it follows from eq 17 and 18 that

$$\left(\frac{\partial\hat{V}_{FH}}{\partial\omega_1}\right)_{\omega_1=0} = \hat{V}_{10} - \hat{V}_1{}^0 + \hat{V}_{FH}(1) - \hat{V}_{FH}(0) \tag{19}$$

Substitution of eq 19 into eq 15 yields the result

$$\frac{1}{D_1{}^0}\left(\frac{\partial D_1}{\partial\omega_1}\right)_{\omega_1=0} = \frac{\gamma\hat{V}_1{}^*}{\hat{V}_2{}^0 f_2}\left[\frac{M_1 f_1\hat{V}_1{}^0}{M_j f_2\hat{V}_2{}^0} + \frac{M_1}{M_j}\frac{(\hat{V}_{10} - \hat{V}_1{}^0)}{f_2\hat{V}_2{}^0} - 1\right] \tag{20}$$

where f_1 and f_2, the fractional hole free volumes of pure solvent and pure polymer, respectively, are defined as follows:

$$f_1 = \hat{V}_{FH}(1)/\hat{V}_1{}^0 \tag{21}$$

$$f_2 = \hat{V}_{FH}(0)/\hat{V}_2{}^0 \tag{22}$$

Since

$$\left(\frac{\partial D_1}{\partial\omega_1}\right)_{\omega_1=0} = \frac{1}{\hat{V}_2{}^0}\left(\frac{\partial D_1}{\partial\rho_1}\right)_{\rho_1=0} \tag{23}$$

it can be easily shown using eq 10, 20, and 23 that F_1 is given by the following result:

$$F_1 = \frac{\gamma\hat{V}_1{}^*}{f_2}\left[\frac{M_1 f_1\hat{V}_1{}^0}{M_j f_2\hat{V}_2{}^0} + \frac{M_1}{M_j}\frac{(\hat{V}_{10} - \hat{V}_1{}^0)}{f_2\hat{V}_2{}^0} - 1\right] \tag{24}$$

To calculate A_2 for a particular polymer-solvent system, it is of course necessary to utilize an explicit expression for the chemical potential of the polymer. This is probably best done using the thermodynamic theory developed by Flory,[14] but the Flory-Huggins theory[15] should be sufficiently accurate for the present purpose and it leads to somewhat simpler results. The Flory-Huggins expression for the chemical potential of the polymer in a polymer-diluent system is simply[15]

$$\mu_2 = \mu_2{}^0 + RT\left[\ln\phi_2 - (1 - \phi_2)\left(\frac{\hat{V}_2{}^0}{\hat{V}_1{}^0} - 1\right) + \chi_1\frac{\hat{V}_2{}^0}{\hat{V}_1{}^0}(1 - \phi_2)^2\right] \tag{25}$$

where ϕ_2 is the volume fraction of the polymer, $\tilde{V}_I^0$ is the molar volume of component I, and χ_1 is the interaction parameter for the particular polymer–solvent system of interest. Hence, from eq 9 and 25, it can be shown that

$$2A_2M_1 = -2\hat{V}_1^0\left(\chi_1 - \frac{\tilde{V}_1^0}{2\tilde{V}_2^0}\right) \tag{26}$$

where the partial specific volumes have been assumed constant to keep eq 26 consistent with the original result of the Flory–Huggins theory.

From the above results, it is evident that the quantity k_D can be determined using the following expression:

$$k_D = -2\hat{V}_1^0\left(\chi_1 - \frac{\tilde{V}_1^0}{2\tilde{V}_2^0}\right) - a_1 - 2\hat{V}_{10} + \frac{\gamma\hat{V}_1^*}{f_2}\left[\frac{M_1f_1\hat{V}_1^0}{M_jf_2\hat{V}_2^0} + \frac{M_1}{M_j}\frac{(\hat{V}_{10} - \hat{V}_1^0)}{f_2\hat{V}_2^0} - 1\right] \tag{27}$$

Consequently, calculation of k_D for a given polymer–solvent system (M_1 and M_2 given) requires the density behavior of the system ($\hat{V}_1^0$, $\hat{V}_2^0$, $\hat{V}_{10}$, a_1), the thermodynamic interaction of the polymer and solvent (χ_1), and the free volume characteristics of the system (γ, M_j, f_1, f_2, $\hat{V}_1^*$). The basic interest here is in the dependence of k_D on f_1/f_2 and M_1/M_j at various free volume conditions for the pure polymer (different values of f_2) and for a solvent with a given value of the specific critical volume, $\hat{V}_1^*$. Hence, for the purpose of illustration, it is assumed that the partial specific volumes are independent of composition so that

$$\hat{V}_{10} = \hat{V}_1^0 \tag{28}$$

$$a_1 = 0 \tag{29}$$

Also, we set $\hat{V}_1^0 = \hat{V}_2^0 = 1$ cm³/g and we let $\tilde{V}_1^0/\tilde{V}_2^0 = 0$ since this is negligible for sufficiently high polymer molecular weights. Since γ is considered to be between ½ and 1, it is set equal to 0.75, and $\chi_1 = 1$ is assumed to be a representative value for the thermodynamic interaction for a typical polymer–solvent system. The choice of a value for χ_1 is not critical. Finally, it is reasonable to expect that the critical amount of local hole free volume per gram necessary for a jump to take place is approximately equal to the specific occupied volume and so we set

$$\hat{V}_1^* = \hat{V}_1^0(0) \tag{30}$$

Again, for illustrative purposes, we consider a class of solvents with $\hat{V}_1^* = \hat{V}_1^0(0) = 1$ cm³/g since this value of $\hat{V}_1^*$ appears to be representative of a large and important group of penetrants. For example, $\hat{V}_1^0(0)$ is 0.946, 1.07, and 0.88 cm³/g for ethylbenzene, water, and ethyl acetate, respectively, as estimated using methods discussed by Haward.[16]

Graphs of k_D vs. f_1/f_2 with M_1/M_j as a parameter are presented in Figures 1 and 2 for two values of the polymeric fractional hole free volume, $f_2 = 0.03$ and $f_2 = 0.09$. These are reasonable values for amorphous polymers in the temperature interval T_{G2} to T_{G2} + 100 °C. The quantity k_D increases with increasing f_1/f_2 since the diffusion process is enhanced as the hole free volume contribution of the solvent increases relative to that of the polymer at fixed f_2. For almost all solvents, $f_1/f_2 > 1$, and large positive values of k_D can be realized since the solvent contributes significantly more free volume than the polymer and, in effect, loosens the polymeric structure. Furthermore, the effect of the solvent on k_D is significantly less for higher values of f_2 (higher temperatures) since the addition of solvent cannot modify the free volume of the system as significantly as it does at lower temperatures where f_2 is much smaller.

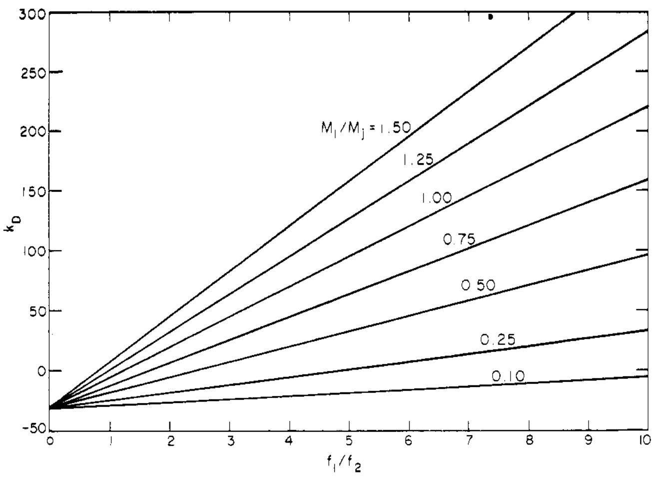

Figure 1. Variation of k_D (cm³/g) with solvent properties for f_2 = 0.03.

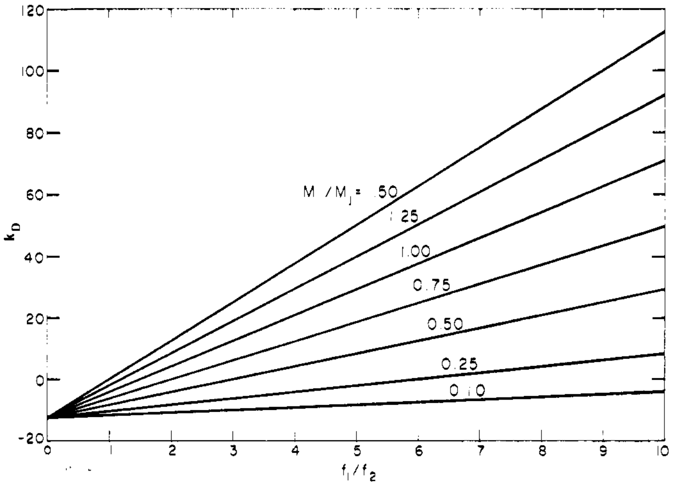

Figure 2. Variation of k_D (cm³/g) with solvent properties for f_2 = 0.09.

These effects can be explained by Fujita's version of the free volume theory and are routinely observed in diffusion experiments on polymer–solvent systems. For example, the poly(methyl acrylate)–ethyl acetate data presented by Fujita[2] show a strong concentration dependence for D near $\rho_1 = 0$, and, furthermore, this concentration dependence becomes less pronounced as the temperature increases. The dependence of k_D on the solvent molecular weight, M_1, is not predicted by the Fujita theory, but, as is evident from Figures 1 and 2, the present theory shows that small molecules of low molecular weight can exhibit a substantially different concentration dependence for D than do solvents with M_1 approximately equal to M_j. For example, for two polymer–solvent systems with equivalent values of f_1 and f_2, the increase in diffusivity with concentration is more pronounced for the system which has the higher molecular weight solvent if the solvents have comparable values of $\hat{V}_1^*$. This result is due to the fact that there are less molecules of the higher molecular weight solvent in the mixture for the same mass fraction, and the increase in D is based on the change in the average hole free volume per molecule.

As a specific example of the effect of solvent size or molecular weight on the concentration dependence of D, we consider some approximate calculations for the poly(methyl acrylate)–water and poly(methyl acrylate)–ethyl acetate systems. It is assumed that the concentration dependence of D for these systems can be adequately represented, for the present purpose, by an equation of the form

$$D = D_0 \exp(\lambda \rho_1) \tag{31}$$

and, hence, $k_D = \lambda$ for these two binary mixtures. Also, it is assumed that a sufficiently accurate value of k_D for the present purpose can be calculated from the following approximate form of eq 27:

$$k_D = \frac{\gamma \hat{V}_1{}^* \hat{V}_1{}^0 f_1}{\hat{V}_2{}^0 f_2{}^2} \left(\frac{M_1}{M_j}\right) \tag{32}$$

For the poly(methyl acrylate)–ethyl acetate system,[2] the diffusivity changes by a factor of approximately 100 at 45 °C in the concentration interval 0 to 0.10 g/cm^3, and a value of $k_D = \lambda = 46$ cm^3/g approximately portrays this concentration dependence. Hence, from eq 32, it follows that k_D or λ is around 10 cm^3/g for the poly(methyl acrylate)–water system, and, consequently, D/D_0 for this system at a concentration of 0.01 g/cm^3 is approximately 1.1. This small change in D is consistent with the data presented by Fujita.[2]

Temperature Dependence of *D*

The temperature dependence of D is conveniently examined by considering D at $\omega_1 = 0$, and, hence, it is necessary to utilize the following result which follows immediately from eq 1:

$$D_0 = D_1{}^0 = D_{01} \exp\left[-\frac{\gamma \xi \hat{V}_2{}^*}{\hat{V}_{\mathrm{FH}(0)}}\right] \tag{33}$$

For a moderate temperature interval above the glass transition temperature of the polymer, it is reasonable to assume that α_{c2} and the thermal expansion coefficient for the polymeric liquid, α_2, can be approximated by average values in the temperature range of interest. Furthermore, for the two expansion coefficients, α_{c2} and α_2, and for the temperature interval under consideration, approximations of the type

$$\exp[\alpha_2(T - T_{G2})] = 1 + \alpha_2(T - T_{G2}) \tag{34}$$

are assumed to give satisfactory accuracy. These assumptions are utilized in a derivation presented elsewhere,[17] and it is shown that $\hat{V}_{\mathrm{FH}}(0)$ can be expressed as

$$\hat{V}_{\mathrm{FH}}(0) = K_{12}(K_{22} + T - T_{G2}) \tag{35}$$

where

$$K_{12} = \hat{V}_2{}^0(T_{G2})[\alpha_2 - (1 - f_{H2}{}^G)\alpha_{c2}] \tag{36}$$

$$K_{22} = \frac{f_{H2}{}^G}{\alpha_2 - (1 - f_{H2}{}^G)\alpha_{c2}} \tag{37}$$

$$f_{H2}{}^G = \frac{\hat{V}_{\mathrm{FH}}(\omega_1 = 0, T = T_{G2})}{\hat{V}_2{}^0(T_{G2})} \tag{38}$$

The effect of solvent size on the temperature dependence of the mutual diffusion coefficient can now be examined both graphically and by the derivation of an equation for the error that results if a linear relationship between the logarithm of D_0 and $1/T$ is utilized. From eq 33 and 35, it can be easily shown that the mutual diffusion coefficients at T and T_{G2} are related by the following expression:

$$\ln\left[\frac{D_0(T)}{D_0(T_{G2})}\right] = \left(\frac{\gamma V_2{}^* \xi}{K_{12}}\right) \frac{T - T_{G2}}{K_{22}(K_{22} + T - T_{G2})} \tag{39}$$

The quantity K_{22} depends on the polymer properties only whereas the quantity $\gamma \hat{V}_2{}^* \xi / K_{12}$ is a function of both the polymer properties and the solvent size since ξ is the ratio of the critical molar volume of the solvent to the critical molar volume of the polymeric jumping unit. Consequently, eq 39 can be used to construct a plot of the logarithm of $D_0(T)/D_0(T_{G2})$ vs. $1/T$ for appropriate values of K_{22} and T_{G2} and for a range of values of $\gamma \hat{V}_2{}^* \xi / K_{12}$, and this plot directly illustrates the effect of solvent size on the temperature dependence of D_0. A plot of this type is presented in Figure 3 with $T_{G2} = 373$ °K and $K_{22} = 45.3$ °K, values which are representative of the properties of polystyrene. The value of K_{22} was deduced from polystyrene–methane diffusion data,[17] and the range for $\gamma \hat{V}_2{}^* \xi / K_{12}$ was suggested by an analysis of polystyrene–solvent diffusion data which showed that this quantity varied from 160 °K for methane to 1030 °K for ethylbenzene. Figure 3 can be considered equivalent to plots of the logarithm of D_0 vs. $1/T$ which are usually constructed from experimental diffusion data on polymer–solvent systems. Some important observations can be made upon consideration of the curves in Figure 3 and these are discussed below.

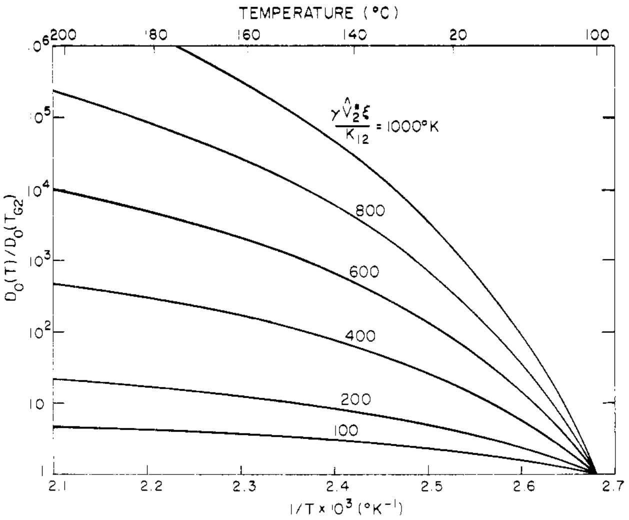

Figure 3. Temperature dependence of D_0 for $T_{G2} = 373$ °K and $K_{22} = 45.3$ °K.

Free volume theory predicts that a plot of the logarithm of D_0 vs. $1/T$ is nonlinear, and a quantitative measure of this nonlinearity can be determined by deriving an expression for the error introduced in D_0 if it is determined in some temperature interval by assuming that the activation energy for diffusion is independent of temperature. An effective or apparent activation energy for diffusion, E_D, can be defined by the equation

$$E_D = RT^2 \left(\frac{\partial \ln D_0}{\partial T}\right)_p \tag{40}$$

and the temperature dependence of E_D predicted by free volume theory is thus given by the following expression:

$$E_D = \frac{RT^2(\gamma \hat{V}_2{}^* \xi / K_{12})}{(K_{22} + T - T_{G2})^2} \tag{41}$$

This result can be used to compare the value of D_0 at a temperature T which is calculated from free volume theory to the diffusivity at T which is calculated by assuming that E_D is constant in an interval extending from some temperature T_1 to T. From eq 41, it can be shown that

$$Q = \exp\left[\frac{(\gamma \hat{V}_2{}^* \xi / K_{12})(T_{G2} - K_{22})(T - T_1)^2}{T(K_{22} + T_1 - T_{G2})^2(K_{22} + T - T_{G2})}\right] - 1 \tag{42}$$

where

$$Q = \frac{[D_0(T)/D_0(T_1)]_{\mathrm{A}}}{[D_0(T)/D_0(T_1)]_{\mathrm{FV}}} - 1 \tag{43}$$

The quantity $[D_0(T)/D_0(T_1)]_{\mathrm{FV}}$ is calculated from free volume theory and the ratio $[D_0(T)/D_0(T_1)]_{\mathrm{A}}$ is determined by assuming that the temperature dependence of D_0 in the interval T_1 to T is described by an Arrhenius expression with an activation energy equal to the free volume result at T_1. Deter-

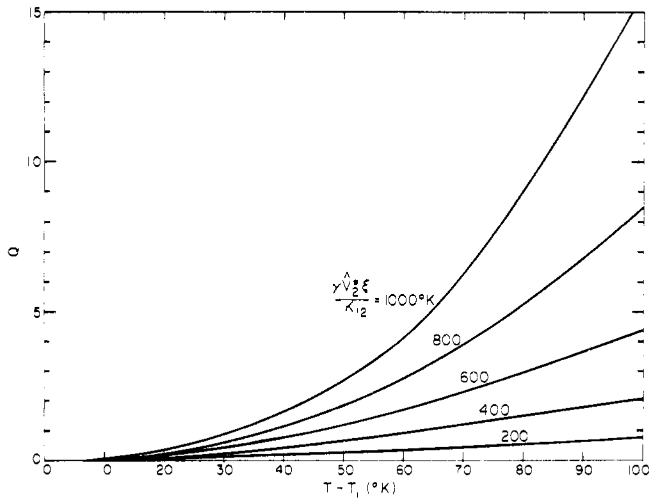

Figure 4. Nonlinearity in temperature dependence of D_0 for T_{G2} = 373 °K, K_{22} = 45.3 °K, and $T_1 - T_{G2}$ = 25 °K.

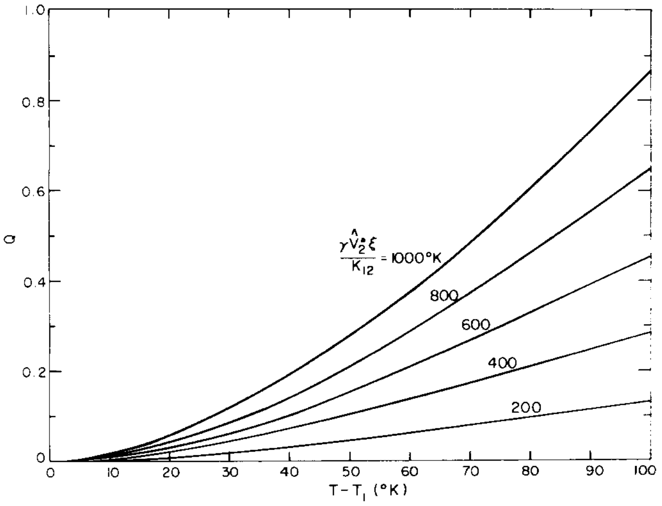

Figure 5. Nonlinearity in temperature dependence of D_0 for T_{G2} = 373 °K, K_{22} = 45.3 °K, and $T_1 - T_{G2}$ = 75 °K.

mination of Q directly illustrates under what conditions a linear relationship for the logarithm of D_0 vs. $1/T$ satisfactorily represents the temperature dependence of D_0 in an interval T_1 to T.

The curves presented in Figures 4 and 5 portray the dependence of Q on the size of the solvent ($\gamma V_2{}^*\xi/K_{12}$), on the temperature interval of interest ($T - T_1$), and on the position of this temperature interval relative to the glass transition temperature of the polymer ($T_1 - T_{G2}$). Although the temperature dependence of D_0 as predicted by free volume theory does not of course lead to a straight line in a logarithm of D_0 vs. $1/T$ plot, it is evident from Figures 3–5 and from eq 42 that a straight line representation becomes satisfactory for sufficiently small temperature intervals, for small solvents, and for temperature intervals sufficiently far above T_{G2}. Since nonlinear behavior is particularly difficult to detect for the diffusion of small solvents over narrow temperature intervals, it is not surprising that Meares[5,6] concluded that plots of the logarithm of D_0 vs. $1/T$ (measured for seven small penetrants) were linear for a temperature interval of 20 °C. The inadequacy of a straight line representation will become apparent even for small solvents when larger temperature intervals are utilized, and, indeed, Kishimoto et al.[3] did observe curvature in the logarithm of D_0 vs. $1/T$ plot for a small penetrant (water) when a larger temperature interval (50 °C) was considered. It is evident from Figures 3–5 that nonlinearities in the logarithm of D_0 vs. $1/T$ plots become easier to detect as the size of the solvent increases, and, as an example of this behavior, Fujita et al.[7] measured a significant variation in E_D for a 30 °C temperature interval when a solvent as large as methanol was utilized.

The above results illustrate that nonlinear behavior in the temperature dependence of D_0 becomes more pronounced as the size of the solvent increases, and, hence, the temperature dependence of D_0 for small solvents can often be satisfactorily represented by an Arrhenius relationship, particularly if the temperature interval is narrow. Furthermore, it should be noted that accurate diffusivity data are needed if the temperature dependence of D_0 is to be examined since, if experimental data scatter significantly, it is of course nearly always possible to justify the construction of a straight line on a logarithm of D_0 vs. $1/T$ plot which adequately portrays the temperature dependence of the diffusivity. Finally, it is fair to conclude that data on the temperature and concentration dependence of D for the diffusion of small penetrants in amorphous polymers can be explained by an appropriate formulation of the free volume theory for polymer–solvent diffusion.

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