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Energy Effects for Solvent Self-Diffusion in Polymer–Solvent Systems

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ABSTRACT: The combined effects of energy and free volume are considered in the self-diffusion of trace amounts of solvents in amorphous polymers. A method for the determination of the parameters of the free-volume theory of transport is discussed. The ability of the combined energy and free-volume formulation to describe the temperature dependence of the self-diffusion process is evaluated using diffusion data both above and below the polymer glass transition temperature.

Introduction

The free-volume theory of transport provides a convenient and useful method of predicting and correlating solvent self-diffusion coefficients for polymer–solvent systems.[1–6] In a general version of the free-volume theory of self-diffusion, it is supposed that the diffusion process depends on the probability that a molecule will obtain sufficient energy to overcome attractive forces and on the probability that a fluctuation in the local density will produce a hole of sufficient size so that the diffusing molecule can jump. The second probability is of course concerned with the availability of sufficient hole free volume for transport to occur. It has generally been assumed that the diffusion process is free-volume driven for temperatures sufficiently close to the glass transition temperature of the system. Consequently, the usual practice has been to focus attention on the free-volume part of the expression for the solvent self-diffusion coefficient, D_1, and to effectively ignore the contribution of the energy part to the temperature dependence of D_1.[5,6]

A recent comprehensive study by Arnould[7] and Arnould and Laurence[8] on the temperature dependence of D_1 for trace amounts of solvents in three polymers indicates that energy effects may be important even for temperatures relatively close to the system glass transition temperature. Consequently, the purpose of this study is to consider the combined effects of free volume and energy in the solvent self-diffusion process. The theory is presented in the second section of the paper, and the application of the theory to the analysis of the data of Arnould[7] and Arnould and Laurence[8] is presented in the third section of the paper.

Theory

The solvent self-diffusion coefficient, D_1, for a rubbery polymer–penetrant mixture can be determined using the following expressions:[1–6]

$$D_1 = D_0 \exp\left[-\frac{E}{RT}\right] \exp\left[-\frac{\gamma(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)}{\hat{V}_{FH}}\right] \quad (1)$$

$$\frac{\hat{V}_{FH}}{\gamma} = \omega_1 \frac{K_{11}}{\gamma}(K_{21} + T - T_{g1}) + \omega_2 \frac{K_{12}}{\gamma}(K_{22} + T - T_{g2}) \quad (2)$$

In these equations, $\hat{V}_I^*$ is the specific hole free volume of component I required for a jump, ω_I is the mass fraction of component I, T_{gI} is the glass transition temperature of component I, 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. In addition, E is the energy per mole that a molecule needs to overcome attractive forces which hold it to its neighbors, D_0 is a constant preexponential factor, $\hat{V}_{FH}$ is the average hole free volume per gram of mixture, and T is temperature. Also, γ is an overlap factor which is introduced because the same free volume is available to more than one jumping unit, K_{11} and K_{21} are free-volume parameters for the solvent, and K_{12} and K_{22} are free-volume parameters for the polymer.

The above free-volume formulation is based on the utilization of the following four assumptions:

(1) The partial specific volumes of the solvent and polymer are independent of composition so that there is no volume change on mixing.

(2) All thermal expansion coefficients are adequately represented by average values over the temperature interval of interest.

(3) The parameter γ is the same over the complete concentration interval.

(4) The energy E is the same for all solvent concentrations.

The first assumption is generally introduced of necessity because volumetric data for polymer–solvent systems are often not available. If the appropriate volumetric data were available, then the first assumption could be eliminated by using a generalized expression for $\hat{V}_{FH}$. All of the data analyzed in this study are in the limit $\omega_1 = 0$ so, for the analysis of this type of data, the first assumption is of course not necessary. The second assumption should be reasonable for the solvent and for the polymer above T_{g2}. Also, this assumption should be an adequate approximation for the thermal expansion coefficient for the liquid polymer for temperatures not too far below T_{g2}. However, for temperatures significantly below T_{g2}, it is probable that the simplification introduced in this assumption will not be valid for the thermal expansion coefficient for the liquid polymer. Some data for solvent self-diffusion in glassy polymers are considered below, but the temperatures considered are reasonably close to T_{g2}. The third assumption is somewhat in question since it has been shown[9] that different materials can have different values of the parameter γ. However, as will be evident from the discussion below, the parameters K_{11}/γ and K_{12}/γ are determined from data for the pure solvent and pure polymer, respectively, so that the correct value of γ is used at the two concentration limits, $\omega_1 = 1$ and $\omega_1 = 0$. Hence, it is reasonable to suppose that significant errors are not introduced for intermediate concentrations. Finally, the fourth assumption is in question since it is quite likely that there will be variations in E over the concentration interval of interest.

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The possibility that the energy E can be a function of the solvent mass fraction has been discussed previously.[5,10-12] It has been noted before[10] that E can change significantly for polymer–solvent systems near $\omega_1 = 1$ as the concentration is changed at fixed temperature. Also, Macedo and Litovitz[11] proposed a concentration dependence for E in the determination of the viscosity of borate mixtures. Furthermore, it has been proposed elsewhere[12] that the concentration dependence of E can be described approximately by considering two energies E_p and E_s. The domains of polymer molecules overlap for solvent mass fractions ranging from 0 to approximately 0.9 or more, and, in this mass fraction range, a solvent molecule sees essentially the same type of surroundings. Hence, E should not change appreciably over this mass fraction interval, and solvent self-diffusion coefficients can be calculated from eq 1 using an essentially constant value of E which can be denoted as E_p. Consequently, for solvent mass fractions roughly in the range of 0–0.9, eq 1 is replaced by the expression

$$D_1 = D_0 \exp\left[-\frac{E_p}{RT}\right] \exp\left[-\frac{\gamma(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)}{\hat{V}_{FH}}\right] \tag{3}$$

Furthermore, as the pure solvent limit is approached, the surroundings of a solvent molecule are changed as polymer molecules become scarce, and the possibility exists that there will be a significant change in E near $\omega_1 = 1$. In general, then, the self-diffusion process in the pure solvent limit may involve a different value of E, denoted as E_s. Hence, if eq 1 is evaluated at $\omega_1 = 1$ using E_s as the energy needed to overcome attractive forces, we arrive at the following expression:

$$D_1 = D_0 \exp\left[-\frac{E_s}{RT}\right] \exp\left[-\frac{\gamma \hat{V}_1^*}{K_{11}(K_{21} + T - T_{g1})}\right] \tag{4}$$

Consequently, in the pure solvent limit, eq 4 can be combined with a relationship between D_1 and the solvent viscosity proposed by Dullien[13] to yield the following expression for the temperature dependence of the viscosity η_1 of the pure solvent:

$$\ln \eta_1 = \ln\left(\frac{0.124 \times 10^{-16} \tilde{V}_c^{2/3} RT}{M_1 \hat{V}_1^0}\right) - \ln D_0 + \frac{E_s}{RT} + \frac{\hat{V}_1^*}{(K_{11}/\gamma)(K_{21} + T - T_{g1})} \tag{5}$$

In this equation, M_1 is the molecular weight of the solvent, $\tilde{V}_c$ is the molar volume of the solvent at its critical temperature, and $\hat{V}_1^0$ is the specific volume of the pure solvent at T.

It is evident that it is in principle possible to use density–temperature and viscosity–temperature data in eq 5 to determine the parameters D_0, E_s, K_{11}/γ, and $K_{21} - T_{g1}$ by applying a nonlinear regression analysis. However, such a procedure does not in general lead to meaningful values of these parameters, presumably because of unacceptable parameter interaction effects.[4] Hence, it seems necessary to replace the $-\ln D_0 + E_s/RT$ term by an average value over the temperature interval. Thus, we introduce a new preexponential factor $\bar{D}_0$ using the approximation

$$-\ln \bar{D}_0 \approx -\ln D_0 + E_s/RT \tag{6}$$

and we suppose that variation of the right-hand side of this equation over moderate ranges of temperature is small since E_s is not generally large for typical solvents.[11] Consequently, it now becomes possible to determine the parameters $\bar{D}_0$, K_{11}/γ, and $K_{21} - T_{g1}$ from eqs 5 and 6 using a nonlinear regression analysis and viscosity and density data for the solvent. In addition, eq 3 can now be written as follows:

$$\ln D_1 = \ln \bar{D}_0 - \frac{E^*}{RT} - \frac{\gamma(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)}{\hat{V}_{FH}} \tag{7}$$

where

$$E^* = E_p - E_s \tag{8}$$

Data presented by Macedo and Litovitz[11] suggest that $E^* > 0$ for a typical polymer–solvent system. Furthermore, evaluation of eq 7 at $\omega_1 = 0$ leads to the important result

$$\ln D_1(\omega_1{=}0) = \ln \bar{D}_0 - \frac{E^*}{RT} - \frac{\gamma \xi \hat{V}_2^*}{K_{12}(K_{22} + T - T_{g2})} \tag{9}$$

which can be rearranged to yield the following expression:

$$Y = E^* + \xi X \tag{10}$$

$$Y = -RT[\ln D_1 - \ln \bar{D}_0] \tag{11}$$

$$X = \frac{RT\left(\dfrac{\gamma \hat{V}_2^*}{K_{12}}\right)}{T + K_{22} - T_{g2}} \tag{12}$$

It is evident from eqs 2 and 7 that determination of the temperature and concentration dependence of D_1 requires the evaluation of nine free-volume and energy parameters: K_{11}/γ, $K_{21} - T_{g1}$, K_{12}/γ, $K_{22} - T_{g2}$, $\hat{V}_1^*$, $\hat{V}_2^*$, $\bar{D}_0$, E^*, and ξ. A semipredictive method for the evaluation of $D_1(\omega_1,T)$ involves the utilization of a small amount of diffusivity data in the evaluation of the nine free-volume parameters and the subsequent calculation of D_1 over wide temperature and concentration ranges. The above development suggests the following semipredictive method for the evaluation of D_1:

(1) The parameters $\hat{V}_1^*$ and $\hat{V}_2^*$ are estimated by equating them to equilibrium liquid volumes at 0 K. Volumes of equilibrium liquids at 0 K can be determined using methods summarized by Haward.[14]

(2) Since WLF constants and glass transition temperatures are available for a large number of polymers,[15] the parameters K_{12}/γ and $K_{22} - T_{g2}$ can be determined by using the following expressions:

$$\frac{K_{12}}{\gamma} = \frac{\hat{V}_2^*}{2.303(C_1^g)_2(C_2^g)_2} \tag{13}$$

$$K_{22} - T_{g2} = (C_2^g)_2 - T_{g2} \tag{14}$$

Here, $(C_1^g)_2$ and $(C_2^g)_2$ are the WLF constants for the polymer. These equations are simply the well-known results relating free-volume parameters and WLF constants.[2-4,10]

(3) The quantities $\bar{D}_0$, K_{11}/γ, and $K_{21} - T_{g1}$ are determined from viscosity–temperature and density–temperature data for the solvent by using a nonlinear regression analysis based on eqs 5 and 6.

(4) Since the mutual diffusion coefficient and the solvent self-diffusion coefficient are equal in the limit $\omega_1 = 0$, it is possible to use a small amount of mutual diffusion data at $\omega_1 = 0$ to construct a Y versus X plot using eqs 10–12. The slope and intercept of this straight line plot yield E^* and ξ. These quantities can of course be calculated with as little as two diffusivity data points.

The procedure proposed above is of course semipredictive because at least two diffusivity data points are needed in the parameter evaluation. These diffusivity data can be obtained using capillary column inverse gas chromatography.[7,8] This technique appears to be a good method of measuring diffusion coefficients at conditions approaching infinite dilution of the solvent. A predictive method for the evaluation of D_1 can be used only if it is assumed that $E^* \approx 0$ and also that the entire solvent molecule is the solvent jumping unit. For this special case, the parameter ξ can be estimated using one of two methods. For the first method, diffusivity data must be available for the diffusion of other solvents (which jump as single units) in the polymer of interest. From these data, the constant β in the following equation can be determined for a particular polymer[16,17]

$$\gamma \hat{V}_2{}^* \xi / K_{12} = \beta \tilde{V}_1{}^0(0) \qquad (15)$$

where $\tilde{V}_1{}^0(0)$ is the solvent molar volume at 0 K. Values of β have been reported for a number of polymers.[16,17] Since $\gamma \hat{V}_2{}^*/K_{12}$ is known from the properties of a particular polymer, it is possible to use eq 15 to compute ξ for solvent diffusion in the polymer of interest for solvents which jump as single units. A second method of estimating ξ has been proposed by Zielinski and Duda.[18] These investigators presented the following empirical linear relationship:

$$\text{molar volume of polymer jumping unit (cm}^3\text{/mol)} = 0.6224T_{g2}\,(\text{K}) - 86.95 \qquad (16)$$

Hence, if T_{g2} is known for the polymer of interest, it is then possible to compute ξ for solvents which jump as single units.

For solvent diffusion at $\omega_1 = 0$ below T_{g2}, the available free volume is given by the expression[19]

$$\frac{\hat{V}_{FH}(\omega_1{=}0)}{\gamma} = \frac{K_{12}}{\gamma}[K_{22} + \lambda(T - T_{g2})] \qquad (17)$$

where the additional parameter λ describes the character of the change of the volume contraction of the pure polymer which can be attributed to the glass transition. Hence, the solvent self-diffusion coefficient at $\omega_1 = 0$ for temperatures below T_{g2} is given by the expression

$$\ln D_1(\omega_1{=}0) = \ln \bar{D}_0 - \frac{E^*}{RT} - \frac{\gamma \xi \hat{V}_2{}^*}{K_{12}[K_{22} + \lambda(T - T_{g2})]} \qquad (18)$$

which can be arranged to yield the following result:

$$W = \lambda(T - T_{g2}) \qquad (19)$$

$$W = -K_{22} - \frac{\dfrac{\gamma \hat{V}_2{}^*}{K_{12}}\xi}{\ln D_1 - \ln \bar{D}_0 + E^*/RT} \qquad (20)$$

Above T_{g2}, it is clear from eq 9 that

$$W = T - T_{g2} \qquad (21)$$

Since λ is a property of the polymer only, λ can be determined using eq 19 and mutual diffusion data for a trace amount of an appropriate solvent in the polymer of interest. The parameters K_{22}, K_{12}/γ, $\hat{V}_2{}^*$, ξ, $\bar{D}_0$, and E^* can be evaluated using the parameter estimation scheme described above. Hence, D_1 versus T data below T_{g2} can be used to form a W versus T plot; the slope of this plot will produce λ. It is clear from eq 21 that the slope of an equivalent plot above T_{g2} should be unity.

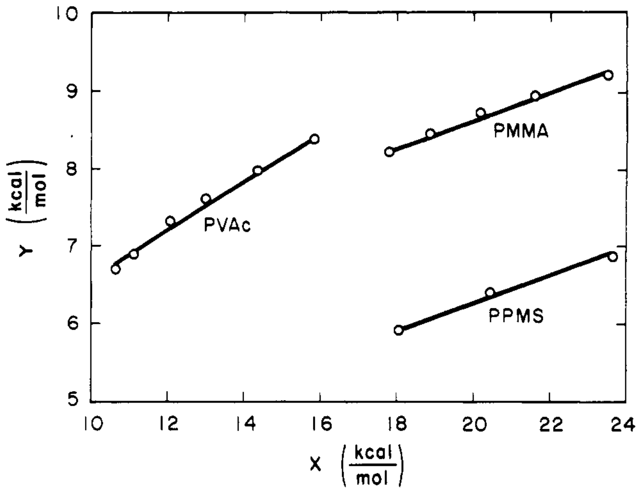

Figure 1. Y versus X plot for methanol diffusion in three polymers. In Figures 1–4, the open circles represent experimental data points.

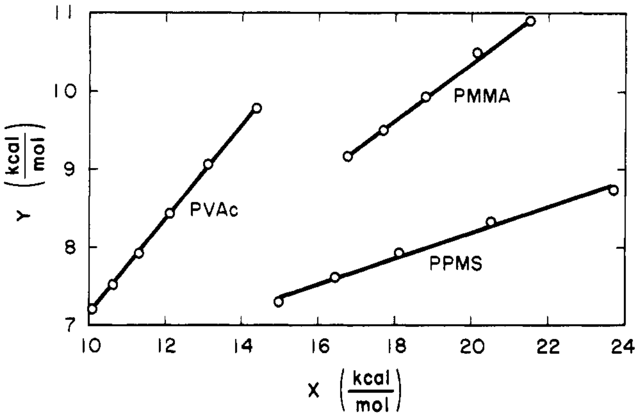

Figure 2. Y versus X plot for acetone diffusion in three polymers.

In this section, we have proposed how free-volume theory can be used to describe the combined effects of free volume and energy in the diffusion process. In particular, eqs 9 and 10 represent the diffusion process for $\omega_1 = 0$ and $T > T_{g2}$, and eqs 18 and 19 represent the diffusion process for $\omega_1 = 0$ and $T < T_{g2}$. These equations are to be used in the determination of the parameters ξ, E^*, and λ. Hence, it is of interest to see if eqs 10 and 19 describe the temperature dependence of $D_1(\omega_1{=}0)$ above and below T_{g2}, respectively. The ability of these equations to describe the experimental temperature dependence of D_1 is considered in the next section.

Results and Discussion

The theory discussed in the previous section is now applied to data involving four solvents (methanol, acetone, toluene, and ethylbenzene) and three polymers [poly(vinyl acetate) (PVAc), poly(methyl methacrylate) (PMMA), and poly(p-methylstyrene) (PPMS)]. Self-diffusion data at $\omega_1 = 0$ for temperatures above T_{g2} for the four solvents in PVAc, PMMA, and PPMS are presented in Figures 1–4. These figures are plots of Y versus X and are based on the D_1–temperature data of Arnould[7] and Arnould and Laurence.[8] In addition to D_1 versus T data, values of $\bar{D}_0$, $K_{22} - T_{g2}$, and $\gamma \hat{V}_2{}^*/K_{12}$ are needed for the construction of these Y versus X plots. Values of these parameters, which were determined using the procedure outlined above, are presented in Tables I and II. It is evident from Figures 1–4 that reasonably good straight lines are obtained in all 12 cases. The linear correlation coefficient and the average absolute error in the linear correlation are presented in

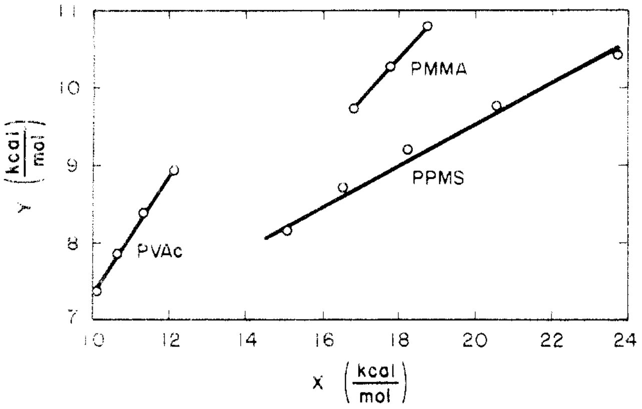

Figure 3. Y versus X plot for toluene diffusion in three polymers.

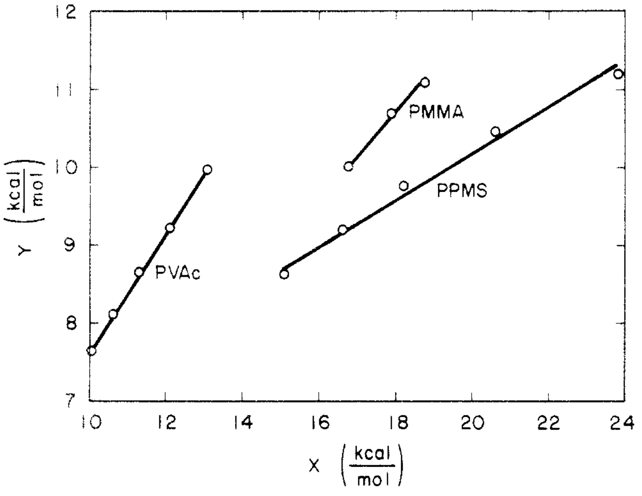

Figure 4. Y versus X plot for ethylbenzene diffusion in three polymers.

Table I
$\hat{D}_0$ Values Needed for Theory Evaluation

solvent	$\ln \hat{D}_0$ (cm^2/s)	solvent	$\ln \hat{D}_0$ (cm^2/s)
methanol	−6.33	toluene	−7.78
acetone	−6.99	ethylbenzene	−7.77

Table II
Polymer Parameters Needed for Theory Evaluation

polymer	$\gamma \hat{V}_2^*/K_{12}$ (K)	$T_{g2} - K_{22}$ (K)	K_{22} (K)
PMMA	2576	308	80
PVAc	1681	256	
PPMS	1658	330	

Table III
Results from Linear Correlation

polymer	solvent	ξ (this study)	ξ (refs 7 and 8)	E^* (kcal/mol)	av absolute error (%)	linear correlation coeff
PMMA	methanol	0.17	0.19	5.3	5.6	0.989
PMMA	acetone	0.38	0.39	2.8	4.5	0.997
PMMA	toluene	0.57	0.54	0.21	2.1	0.999
PMMA	ethylbenzene	0.51	0.54	1.7	6.4	0.990
PVAc	methanol	0.32	0.31	3.4	9.5	0.993
PVAc	acetone	0.61	0.60	1.0	3.0	0.999
PVAc	toluene	0.76	0.75	−0.24	2.0	0.999
PVAc	ethylbenzene	0.77	0.78	−0.11	3.2	0.999
PPMS	methanol	0.16	0.15	3.1	6.9	0.988
PPMS	acetone	0.16	0.15	5.0	9.8	0.986
PPMS	toluene	0.26	0.23	4.4	14	0.990
PPMS	ethylbenzene	0.29	0.26	4.4	14	0.990

Table III. The average absolute error represents the average difference between the data and the values of D_1 computed from the linear correlation. Since the linear correlation coefficient ranges from 0.986 to 0.999 and since the worst average error is 14%, it seems reasonable to conclude that free-volume theory provides a good representation of the diffusivity data when the energy term is included.

The linear plots in Figures 1–4 produce values of E^* and ξ for each system, and the values of these parameters are reported in Table III. Values of E^* are generally higher for solvent self-diffusion in PPMS. The values of ξ determined from the Y–X plots are compared with the ξ values reported by Arnould[7] and Arnould and Laurence[8] in Table III. There is reasonably good agreement between the two sets of values. The ξ values determined in this study were computed using all of the self-diffusion data above T_{g2}, whereas Arnould and Arnould and Laurence sometimes had to use only the lower temperature data in their calculation of ξ. They considered only the free-volume contribution in their analysis, and the diffusion process becomes free-volume driven as the temperature is decreased. In the analysis presented here, free-volume and energy effects are considered simultaneously so that there is no restriction on the temperature range.

It has been noted previously[20] that $\gamma \hat{V}_2^* \xi / K_{12}$ (and hence ξ) should be a linear function of the molar volume at 0 K of the solvent jumping unit for diffusion in a particular polymer. In general, it is possible to construct such linear plots for solvents for which the entire solvent molecule performs a jump by plotting $\gamma \hat{V}_2^* \xi / K_{12}$ or ξ versus the solvent molar volume at 0 K. The slope of this type of plot yields the constant β in eq 15. Arnould[7] and Arnould and Laurence[8] noted that their diffusivity data were consistent with the free-volume picture of solvent size with one exception, methanol diffusion in PPMS. They showed that small or spherically shaped solvents exhibited ξ values which depended linearly on the solvent molar volume at 0 K. The ξ values for larger and more flexible solvents fall below this straight line, presumably because of the segmental motion of these solvents. For methanol diffusion in PPMS, the value of ξ is considerably above the straight line constructed using data for other solvents for which it is reasonable to expect that the entire molecule performs a jump. It is clear from Table III that the present analysis does not resolve this anomaly since our ξ value is virtually identical to that reported by Arnould.[7] There seems to be no obvious explanation for this inconsistency. It is also important to note that the molar volume of the polymer jumping unit for PPMS is estimated to be about 380 cm^3/mol (based on acetone–PPMS diffusion data). The empirical correlation of Zielinski and Duda[18] gives an estimate of 148 cm^3/mol. Hence, the Zielinski–Duda correlation does not appear to be consistent with most of the PPMS–solvent diffusivity data. If it is supposed that methanol is the only solvent to jump as a single unit in PPMS, then the molar volume of the polymer jumping unit is 196 cm^3/mol.

The solvent self-diffusion process below T_{g2} at $\omega_1 = 0$ was examined using diffusivity data for the methanol–PMMA system.[7] A plot of W versus temperature was constructed for this system using the reported diffusivity data and known values of $\gamma \hat{V}_2^*/K_{12}$, $\hat{D}_0$, K_{22}, ξ, and E^*. Values of these parameters are presented in Tables I–III. The plot of W versus temperature for the methanol–PMMA system is presented in Figure 5. Several observations can be made about this W–T plot. First, the data are reasonably well represented by eq 19 for temperatures below T_{g2} and by eq 21 for temperatures above T_{g2}. The slope of the straight line below T_{g2} gives a value of $\lambda = 0.40$ for the methanol–PMMA system. It was previously noted[19] that an upper bound for λ for PMMA was 0.41.

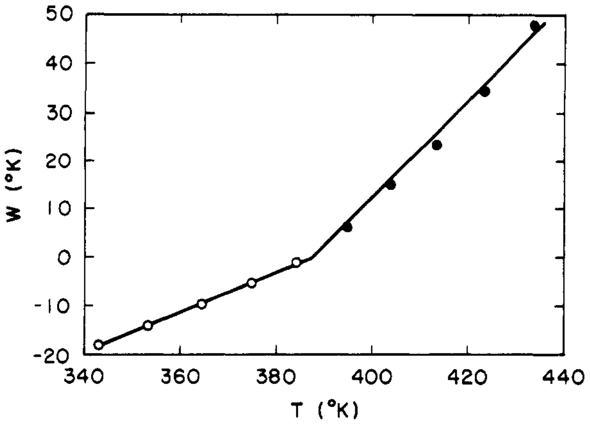

Figure 5. W versus temperature plot for methanol diffusion in PMMA. The solid circles represent experimental data points above T_{g2}, and the open circles represent data points below T_{g2}. The straight line above T_{g2} has a slope of unity, and the straight line below T_{g2} has a slope of $\lambda = 0.40$.

From the above results, it is fair to conclude that a free-volume theory which considers the combined effects of free volume and energy provides a reasonably good representation of the temperature dependence of D_1 over temperature ranges for which D_1 changes by as much as 2 orders of magnitude. A pure free-volume correlation or a pure energy correlation (an Arrhenius equation) can also provide adequate representations of the temperature dependence of D_1 over moderate temperature ranges. However, it is reasonable to expect that the combined energy and free-volume formulation should provide better results over a wider range of conditions. For example, for the acetone–PVAc system, the present theory has an average absolute error of 3% and the Arrhenius correlation has an average absolute error of 13%. The acetone–PVAc system has a reasonably small energy term so that the Arrhenius equation does not do as well as the combined theory when a reasonably large temperature range is considered. The utilization of a free-volume theory which considers both energy and free-volume effects does require at least two diffusivity data points. However, perhaps it will prove possible to generate such data using a molecular simulation of the diffusion of a trace of solvent in the polymer.

Finally, it seems useful to review some of the assumptions in the above development. Some of these assumptions have been widely utilized since they are reasonable approximations. For example, the utilization of average values for thermal expansion coefficients leads to less than 1% error in calculated volumes over a temperature range of 100 °C. In addition, the estimation of $\hat{V}_1^*$ and $\hat{V}_2^*$ is quite reasonable since the hole free volume required for a jump should be equal to the volume that a molecule occupies.[1] The best estimate for the occupied volume is the liquid volume at 0 K. Justification has also been provided previously[12] for the approximation used in estimating the concentration dependence of the energy term. Although the approximate variation in magnitude of the energy over the entire concentration interval is E^*, it is of course not possible to determine the actual concentration dependence of the energy over the concentration interval since any meaningful calculation must necessarily assume that free-volume theory otherwise does a perfect job of predicting the concentration dependence. The concentration variation is thus idealized by assuming that the concentration dependence is described by two energies, E_p and E_s. There are indications[12] that an apparently anomalous concentration dependence exists for high penetrant concentrations, and this implies a change in the energy near the pure solvent limit ($\omega_1 > 0.9$). This gives some creditability to the two-energy model, which provides a reasonable basis for including energy effects. It is evident from previous work[7,8] that diffusivity predictions are sensitive to the presence or absence of an energy term. Another important approximation is the utilization of eq 6. This approach is necessitated by the diffculty in determining values of D_0 and E_s using eq 5 and a nonlinear regression analysis on density–temperature and viscosity–temperature data. Indeed, as noted previously,[4] such a procedure yields free-volume parameters which are as much as 5 times larger than upper bound estimates. Utilization of eq 6 in eq 5 produces an equation which provides a very good representation of the viscosity and density data over the temperature range of interest. The errors introduced in step 3 of the procedure for estimating D_1 are not presented here since the errors introduced in the *entire* evaluation procedure are presented in Table III. Finally, the values of E^* presented in Table III indicate that E_p and E_s are similar in magnitude, but this is simply because both E_p and E_s are not particularly large.[11]

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