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Free Volume at the Glass Transition Point

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Recently, Frick et al.[1] have made an important finding from measurements of the tracer diffusion coefficient of a dye (Aberchrome 540) dispersed in toluene solutions of polystyrene. According to this finding, this polymer/solvent system does not obey the rule of thumb that the glass transition occurs at an isofractional free volume. They analyzed their experimental data using an extended version[2] of the Vrentas–Duda free volume theory of diffusion[3] and made clear the shortcomings as well as the advantages of the new theory. The present paper approaches the same data from the free volume theory of Fujita[4] in order to see how the fractional free volume at the glass transition temperature varies as polystyrene is diluted with toluene.

Fractional Free Volume at the Glass Transition Point. The system we consider consists of Aberchrome 540 (AB) trace-dispersed in a solution of monodisperse polystyrene (PS) and toluene (TL). We denote the weight fraction of toluene by w_s and the fractional free volume in the solution by f. The concentration of AB is so small that f may be treated as depending only on w_s and the temperature T. The free volume theory of Fujita[4] postulates that $f(T,w_s)$ controls the mobilities of AB, TL, and a segment of PS (denoted m_{AB}, m_{TL}, and m_{PS}, respectively) according to expressions of the Doolittle type[5]

$$\ln m_{AB} = C_{AB} - B_{AB}/f(T,w_s) \tag{1}$$

$$\ln m_{TL} = C_{TL} - B_{TL}/f(T,w_s) \tag{2}$$

$$\ln m_{PS} = C_{PS} - 1/f(T,w_s) \tag{3}$$

where C and B are constants characteristic of the respective species. Note that the B coefficient for the PS segment is chosen to be unity without loss of generality and that eq 3 should be regarded as the defining equation for f in the framework of the Fujita theory.

We denote by $T_g(w_s)$ the temperature at which the system with a composition of w_s undergoes the glass transition and represent f in that solution at $T_g(w_s)$ by $f_g(w_s)$. Our first assumption is that, if it occurs, the deviation of $f_g(w_s)$ from the value at $w_s = 0$, i.e., $f_g(0)$, is proportional to the distance that $T_g(w_s)$ is apart from $T_g(0)$. Mathematically, this is represented by

$$f_g(w_s) = f_g(0) + A[T_g(0) - T_g(w_s)] \tag{4}$$

with A as an unknown proportionality factor. We may expect eq 4 to be adequate if the solution is not much removed from pure PS.

Substituting eq 4 into eq 1 at the composition w_s and the temperature $T_g(w_s)$, using the Einstein relation $D_{AB} \propto Tm_{AB}$, and denoting D_{AB} at w_s and $T_g(w_s)$ by $D_{AB}^{g}(w_s)$, we can derive the relation

$$\ln\left[\frac{D_{AB}^{g}(w_s^*)}{D_{AB}^{g}(w_s)}\right] = -\ln\left[1 + \frac{\Delta(w_s)}{T_g(w_s^*)}\right] + \frac{B_{AB}A\Delta(w_s)}{[f_g(0) + A(T_g(0) - T_g(w_s^*))][f_g(0) + A(T_g(0) - T_g(w_s^*)) - A\Delta(w_s)]} \tag{5}$$

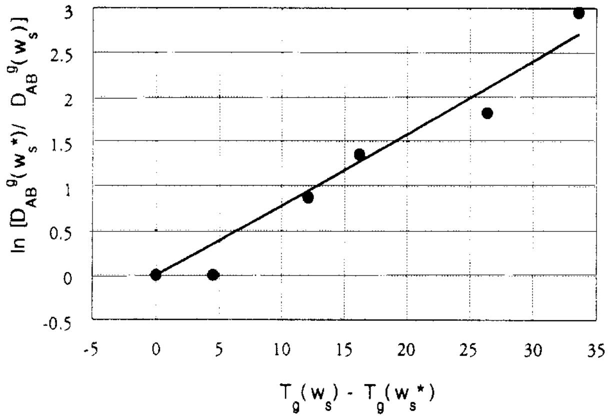

Figure 1. Dye diffusion coefficient D_{AB}^{g} at the glass transition as a function of the glass transition temperature $T_g(w_s)$ (in K) for toluene solutions of polystyrene. Filled circles are data by Flick et al.[1] The solid line is computed by eq 5.

where

$$\Delta(w_s) = T_g(w_s) - T_g(w_s^*) \tag{6}$$

and w_s^* denotes w_s in an arbitrarily chosen reference PS/TL solution.

We assign 0.0300, instead of the usual value 0.025, to $f_g(0)$ to make eq 2 with $B_{TL} = 0.54$ consistent with the data of Pickup and Blum[6] for the toluene self-diffusion coefficient in the PS/TL system (see below). This value is not unreasonable because a comparably high value of 0.032 is cited for polystyrene in Ferry's book (p 277).[7] We choose 105 °C as a best value for $T_g(0)$ for PS. Furthermore, we take $w_s^* = 0.201$ as the reference composition at which Frick et al.[1] found $\log D_{AB}^{g} = -13.35$ and $T_g = -4.2$ °C. We find from their paper that $B_{TL} = 0.54$ and $B_{AB}/B_{TL} = 4.92$, so that $B_{AB} = 2.26$, using the formal equivalence of the B coefficient in the Fujita theory to the parameter ξ in the Vrentas–Duda theory.[3] According to many studies by Duda and associates, as summarized by Zielinski and Duda,[8] ξ is generally smaller than unity. Thus, the value of B_{AB} found by Frick et al.[1] has to be considered unusually large. However, the reason why it happened is beyond the current scope of free volume theory.

With the above assignments, eq 5 contains only a single paramter A. We have sought a value of A that would give a best fit of eq 5 to the D_{AB}^{g} data of Frick et al. by using the software Kaleidagraph for the Macintosh. The resulting fit is shown in Figure 1, which gives $A = 4.28 \times 10^{-5}/°\text{C}$. Not much importance should be given to this numerical value, because the evaluation of A is sensitive to the choice of $f_g(0)$. The A value obtained implies that the fractional free volume at the glass transition for the PS/toluene system is not independent of solution composition but increases by 0.0043 for a 100 °C decrease in T_g. In the range of w_s from 0.119 to 0.201 studied by Frick et al., $f_g(w_s)$ changes by 0.0015, that is, only 5% of $f_g(0)$. Nonetheless, the corresponding change in the measured D_{AB}^{g} amounts to 3 orders of magnitude. This surprising correlation between the changes in f_g and D_{AB}^{g} suggests how sensitively the glass transition is affected by the free volume. Obviously, no free volume theory is able to explain why the rule of thumb for f_g breaks down in the PS/toluene system.

Composition Dependence of the Glass Transition Temperature. Recently, Fujita and Einaga[9] (see also Fujita[10]) have shown for typical polymer/solvent systems well above their T_g that the fractional free volume f varies

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linearly with ϕ_s up to a fairly high solvent composition, where ϕ_s is the volume fraction of the solvent component. If we assume no volume change on mixing, this relation is written in terms of w_s as

$$f(T,w_s) = f_p(T) + \frac{v_s[f_s^*(T) - f_p(T)]w_s}{v_p + (v_s - v_p)w_s} \qquad (7)$$

where v_s and v_p are the specific volumes of the solvent and polymer components, respectively, $f_p(T)$ is the fractional free volume in the pure polymer, and $f_s^*(T)$ is a parameter that represents the fractional free volume of the solvent trapped in the polymer matrix. Actually, the difference of the latter from the fractional free volume of the pure solvent reflects the effect that the solvent mobility in highly concentrated solutions undergoes from the entangled polymer chains, i.e., the polymer–solvent interaction in such systems. The Fujita theory takes this interaction into account by leaving $f_s^*(T)$ as a quantity to be evaluated from experimental data.

To extract more information from eq 4, we assume that eq 7 is valid down to $T_g(w_s)$ of a given solution and invoke the idea used by Vrentas et al.[2] in their formulation of an extended version of the Vrentas–Duda free volume theory. The idea is that when a polymer solution is cooled, the polymer in it is not frozen at $T_g(0)$ but maintains the rubbery state down to $T_g(w_s)$. It implies that in the temperature range where $f(T,w_s) > f(T_g(w_s))$, the fractional free volume $f_p(T,w)$ associated with the polymer in the solution behaves like that in equilibrium polymer/solvent systems even when $T < T_g(0)$. It has been shown[10] that $f_p(T,w)$ can be equated to $f_p(T,0)$, i.e., $f_p(T)$ defined above, in the compositional range where eq 7 holds. Thus, following the idea of Vrentas et al., we may proceed with eq 7 in which $f_p(T)$ is expressed by

$$f_p(T) = f_p(T_g(0)) - \alpha[T_g(0) - T] \quad (T > T_g(w_s)) \qquad (8)$$

where α is the thermal expansion coefficient of $f_p(T)$ for the rubbery polymer.

The solvent in concentrated polymer solutions may be far above its glass transition temperature at $T > T_g(w_s)$. Therefore, it is reasonable to represent $f_s^*(T)$ in eq 7 by

$$f_s^*(T) = f_s^*(T_g(0)) - \epsilon[T_g(0) - T] \qquad (9)$$

with ϵ denoting the thermal expansion coefficient of $f_s^*(T)$.

Now, we substitute eqs 8 and 9 referring to $T = T_g(w_s)$ into eq 7 and note that $f(T_g(w_s),w_s)$ and $f_p(T_g(0))$ are, respectively, the same as $f_g(w_s)$ and $f_g(0)$ defined earlier. The result is

$$f_g(w_s) = f_g(0) - \alpha[T_g(0) - T_g(w_s)] + \frac{v_s\{[f_s^*(0) - f_g(0)] - (\epsilon - \alpha)[T_g(0) - T_g(w_s)]\}w_s}{v_p + (v_s - v_p)w_s} \qquad (10)$$

where $f_s^*(0)$ denotes $f_s^*(T_g(0))$. With eq 10, eq 4 can be solved for $T_g(0) - T_g(w_s)$ to give

$$T_g(w_s) = T_g(0) - \frac{Lw_s}{1 + Kw_s} \qquad (11)$$

where

$$L = (v_s/v_p)(f_s^*(0) - f_g(0))/(A + \alpha) \qquad (12)$$

$$K = (v_s/v_p)(\epsilon - \alpha)/(A + \alpha) + (v_s/v_p) - 1 \qquad (13)$$

Equation 11 gives the composition dependence of the glass transition temperature predicted on the assumptions made above. With $T_g(0)$ taken to be 105 °C, we have again used the software Kaleidagraph for the Macintosh to fit eq 11 to the $T_g(w_s)$ data given in the paper of Frick et al.[1] The solid line in Figure 2 shows the result and gives $L = 880$ °C and $K = 2.64$.

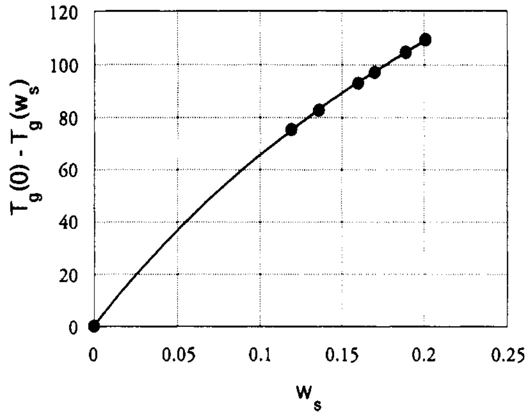

Figure 2. Dependence of the glass transition temperature T_g (in K) on toluene weight fraction w_s. Filled circles are data taken from Frick et al.[1] The solid line is calculated by eq 11.

Fractional Free Volume for PS at the Glass Transition Point. We have assigned 0.0300 to $f_g(0)$ for analyzing the D_{AB} data of Frick et al. We now show how this value was derived.

At $T = T_g(0)$ eq 7 gives

$$f(T_g(0),w_s) = f_g(0) + \frac{v_s[f_s^*(0) - f_g(0)]w_s}{v_p + (v_s - v_p)w_s} \qquad (14)$$

Combining this expression with eq 2 and using the Einstein relation $D_{TL} \propto Tm_{TL}$, we can derive

$$\frac{w_s - w_s^*}{\ln[D_{TL}(w_s)/D_{TL}(w_s^*)]} = I + S(w_s - w_s^*) \qquad (15)$$

where w_s^* is a reference composition taken below as 0.114, and

$$I = [v_p f_g(0) + E w_s^*]^2/(B_{TL} v_s v_p C) \qquad (16)$$

$$S = [v_p f_g(0) + E w_s^*]E/(B_{TL} v_s v_p C) \qquad (17)$$

with

$$C = f_s^*(0) - f_g(0) \qquad (18)$$

$$E = v_s f_s^*(0) - v_p f_g(0) \qquad (19)$$

Equation 15 predicts that the left-hand side plotted against $w_s - w_s^*$ falls on a straight line. When substituted into eqs 16 and 17, the intercept I and slope S of the line allow evaluation of $f_g(0)$ and $f_s^*(0)$ if B_{TL} is known in advance along with v_s and v_p.

Figure 3 shows the predicted linear relation with the data of Pickup and Blum[6] at $T = 105$ °C, i.e., $T_g(0)$. With $v_s = 1.29$ (in cm^3/g) and $v_p = 0.952$ (in cm^3/g) at this temperature given by these authors along with $B_{TL} = 0.54$ mentioned earlier, we can derive the following values from the indicated line ($I = 0.030$, $S = 0.186$): $f_g(0) = 0.0289$ and $f_s^*(0) = 0.472$. The determination of these parameters depends sensitively on the choice of B_{TL} as well as the D_{TL} data used. Hence, we have rather arbitrarily chosen 0.030 for $f_g(0)$ in the above analysis of the Frick et al. data.

With these values of $f_g(0)$ and $f_s^*(0)$ along with those of A, L, and K evaluated above we can calculate the parameters α and ϵ from eqs 12 and 13. The results are $\alpha = 7.1 \times 10^{-4}$/°C and $\epsilon = 1.98 \times 10^{-3}$/°C. This α value is consistent with (6–7) $\times 10^{-4}$/°C as cited for polystyrene

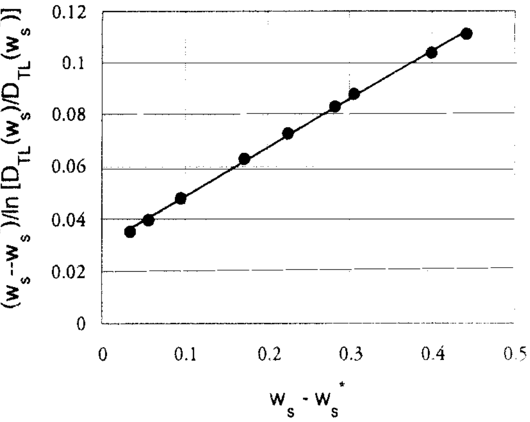

Figure 3. Self-diffusion coefficient D_{TL} in the PS/TL system at $T_g(0)$ as a function of toluene weight fraction w_s. Filled points are data of Pickup and Blum.[6] The solid line is the predicted linear relation.

in Ferry's book[7] (p 277). The ϵ value also falls in the order of magnitude for simple liquids.

Discussion. Apart from eqs 1–3 basic to the free volume theory of Fujita, the underlying assumptions of the present analysis are (a) that eq 4 relates the change in the fractional free volume at T_g linearly to the decrease in T_g with w_s, (b) that eq 7 describes the composition dependence of the fractional free volume, and (c) that, according to Vrentas et al., the polymer in a concentrated solution maintains the rubbery state down to the glass transition temperature of the solution. The last assumption allows $f_p(T)$ in eq 7 to be represented by eq 8 for $T > T_g(w_s)$. However, eq 8 gives $f_p(T)$ physically unacceptable negative values below a certain temperature when $T_g(w_s)$ is much lower than $T_g(0)$. Thus, the present theory is essentially concerned with solutions of low solvent concentrations.

Using the parameter values that Vrentas et al.[11] have determined to fit the Vrentas–Duda theory to the data of Pickup and Blum,[6] we calculate $f_s(T_g(0))$, the fractional free volume in pure toluene at 105 °C, to be 0.493, and $f_p(T_g(0))$, i.e., $f_g(0)$, to be 0.0337 (see the Appendix). These values compare with $f_s^*(0) = 0.472$ and $f_g(0) = 0.0289$ from our analysis. The relation $f_s^*(0) < f_s(T_g(0))$ implies that toluene has a smaller free volume in the polystyrene matrix than in pure liquid and is consistent with what Fujita and Einaga[9,10] have supposed to be a general trend on the basis of viscosity data on typical amorphous polymer/solvent systems. However, the difference between $f_s^*(0)$ and $f_s(T_g(0))$ is much smaller than those in the systems analyzed by Fujita and Einaga.

Appendix. We consider pure toluene liquid. As has been discussed recently,[10] eq 2 is not adequate for the analysis of its dynamic behavior, but the factor B_{TL} must be replaced by unity, since otherwise the Einstein–Stokes relation is not obeyed for the polymer molecule at infinite dilution. Thus, the Fujita free volume theory should be modified appropriately as the dilution approaches a certain stage. This point is not characteristic of the Fujita theory but also appears in the Vrentas–Duda theory (as seen from comparison of eqs 13 and 14 of Vrentas and Duda[3]).

If toluene obeys the WLF equation (Ferry,[7] p 287), application of eq 2 with $B_{TL} = 1$ to viscosity data as a function of temperature allows evaluation of the WLF constants c_1 and c_2 in the expression

$$f_s(T) = (1/2.303)[(c_1)^{-1} + (c_1c_2)^{-1}(T - T_g(1))] \quad (1a)$$

where $f_s(T)$ denotes f for pure toluene at temperature T. According to Vrentas and Duda,[12] c_1 and c_1c_2 are expressed in terms of the characteristic parameters of their theory as

$$2.303c_1 + \gamma\hat{v}_s^*/(K_{11}K_{21}) \quad (2a)$$

$$2.303c_1c_2 = \gamma\hat{v}_1^*/K_{11} \quad (3a)$$

where γ, K_{11}, and K_{12} are constants, and $\hat{v}_s^*$ is the critical specific hole volume for the jump of a solvent molecule. Thus, eq 1a can be rewritten as

$$f_s(T) = (K_{11}/\gamma\hat{v}_s^*)[K_{21} + T - T_g(1)] \quad (4a)$$

Substituting the toluene data reported by Vrentas et al.[11] that give $\hat{v}_s^*$ (in cm^3/g) = 0.917, K_{11}/γ (in cm^3/g °C) = 0.001 57, and $K_{21} - T_g(1)$ (in °C) = 182.65, we get $f_s(1) = 0.493$ at 100 °C, as quoted above.

Corresponding to eq 4a, we have, for $f_p(T)$, the fractional free volume in pure polymer at temperature T,

$$f_p(T) = (K_{12}/\gamma\hat{v}_p^*)[K_{22} + T - T_g(0)] \quad (5a)$$

After attempting to fit the Vrentas–Duda theory to the data of Pickup and Blum,[6] Vrentas et al.[11] reached the numerical results: $\hat{v}_p^*$ (in cm^3/g) = 0.850, K_{12}/γ (in cm^3/g °C) = 0.000582, and $K_{22} - T_g(0)$ (in °C) = −53.85. Thus, eq 5a gives $f_g(0) = 0.0337$, which is also quoted above. Frick et al.[1] derived 0.000223 instead of 0.000582 for K_{23}/γ, but very recently Vrentas and Vrentas[13] pointed out the former to be inadequate.

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