Free volume analysis of the viscosity of concentrated polymer solutions

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(Received 7 August 1989; revised 5 September 1989; accepted 11 September 1989)

The fractional free volume f of a polymer solution as a function of temperature T and polymer volume fraction ϕ_p is expressed as $f(T, \phi_p)=f_p^0(T)\phi_p+f_s(T, \phi_p)(1-\phi_p)$, and f_s, the fractional free volume of the solvent, in the entangled region is determined from viscosity data on some typical polymer + solvent systems by using the established empirical relation η(viscosity)$\sim\zeta_p\phi_p^{3.5}M_w^{3.5}$. Here, ζ_p is the friction coefficient of a polymer jumping unit and related to f by $\zeta_p\sim\exp(1/f)$. For all the systems examined, which include both rubbery and glassy polymers, f_s is virtually independent of ϕ_p in entangled solutions, but, except for one system, it is much smaller than f_s^0, the solvent fractional free volume in the pure state. This finding shows that the additivity in the fractional free volume, i.e., the relation $f=f_p^0\phi_p+f_s^0(1-\phi_p)$ does not hold in general. The concentration dependence of η of entangled polymer solutions is essentially governed by f_p^0 and f_s^*, the latter being f_s at the limit $\phi_p\to 1$.

(Keywords: free volume analysis; viscosity; polymer solutions)

INTRODUCTION

Though classic, the dependence of the steady shear viscosity η (hereafter referred to as the viscosity for simplicity) of concentrated polymer solutions on concentration is still a subject of considerable interest. Its quantitative interpretation in terms of the free volume concept yet leaves something to be desired. Fujita and Kishimoto[1] applied this concept to formulating η of (quasi-binary) polymer solutions as a function of concentration. They focused on solutions in which the molecular weight dependence of η obeys the 3.4 power empirical law and started from the expression

$$\eta=KM_w^{3.4}\phi_p\zeta_p(T, \phi_p) \tag{1}$$

Here, M_w and ϕ_p are the weight-average molecular weight and the volume fraction of the polymer, respectively, $\zeta(T, \phi_p)$ the friction coefficient per polymer segment as a function of temperature T and ϕ_p, and K a parameter independent of T, ϕ_p, and M_w. Fujita and Kishimoto[1] then introduced the fractional free volume $f(T, \phi_p)$ defined by

$$\zeta_p=A_p\exp[1/f(T, \phi_p)] \tag{2}$$

where A_p is a proportionality factor. This definition tells nothing of the physical picture of f and hence it is largely frustrating.

Finally, the Fujita and Kishimoto (FK) theory assumed that when a solvent is mixed with an undiluted polymer, f increases by an amount proportional to the volume fraction of the added solvent. Mathematically, this assumption is expressed by

$$f(T, \phi_p)=f_p^0(T)+\beta'(T)(1-\phi_p) \tag{3}$$

where f_p^0 is the fractional free volume in the undiluted polymer (in the following, the superscript 0 is used to signify the pure state of either polymer or solvent) and the proportionality factor $\beta'(T)$ may depend on both solvent and polymer. If equation (3) holds down to $\phi_p=0$, $\beta'(T)$ can be equated to $f_s^0(T)-f_p^0(T)$, where $f_s^0(T)$ is the fractional free volume in the pure solvent, and equation (3) may be written

$$f(T, \phi_p)=f_p^0(T)\phi_p+f_s^0(T)(1-\phi_p) \tag{4}$$

This equation was assumed by Kelley and Bueche[2] to formulate a free volume theory of η, which was published in the same year when the FK theory appeared.

It is important to distinguish equation (3) from equation (4). The FK theory treated $\beta'(T)$ as an empirical function of T which has to do with the effectiveness of the added solvent for the change in f, as pointed out by Frisch *et al.*[3]. In their criticism on the free volume theory of Fujita *et al.*[4,5] for the diffusion of diluents in polymer solids, Vrentas and Duda[6,7] apparently misunderstood that Fujita *et al.*[4,5] had assumed equation (4) for f. However, what Fujita *et al.*[4,5] assumed is equation (3), as in the FK theory for viscosity. Actually, it is quite plausible that, in entangled solutions, the fractional free volume of the solvent undergoes a considerable effect from the coexisting polymer molecules. Hence, equation (4) ought to be inadequate for such systems.

The present paper attempts to examine the approximation of equation (3) to solutions of linear amorphous polymers in the concentrated regime by analysing some reported viscosity data on such polymers. In actuality, we rewrite equation (3) as

$$f(T, \phi_p)=f_p^0(T)\phi_p+f_s(T, \phi_p)(1-\phi_p) \tag{5}$$

and evaluate $f_s(T, \phi_p)$ as a function of ϕ_p. The new quantity $f_s(T, \phi_p)$ may be referred to as the fractional free volume of the solvent in the solution of temperature T and concentration ϕ_p.

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0032-3861/90/081486-05

METHOD OF ANALYSIS

According to the detailed study of Berry and Fox[8], it is more adequate to express η not by equation (1) but as the product of ζ_p and a factor F scaled by a dimensionless molecular weight M_w/M_c, i.e.,

$$\eta = \zeta_p(T, \phi_p)F(M_w/M_c(\phi_p)) \tag{6}$$

Here, $M_c(\phi_p)$ is the critical molecular weight above which F at fixed ϕ_p increases with M_w according to an empirical power law $F \sim M_w^{\nu}$ with $\nu = 3.5 \pm 0.2$ (here we do not ask the molecular mechanism responsible for this surprisingly general law). Experimentally, this molecular weight as a function of ϕ_p is fitted by

$$M_c(\phi_p) = M_c^0/\phi_p \tag{7}$$

where M_c^0 is the value of M_c for the undiluted polymer. Thus, with ν taken to be 3.5 (instead of the familiar 3.4 for no special reason), we may assume for a given polymer that the relation

$$\eta = K'\zeta(T, \phi_p)\phi_p^{3.5}M_w^{3.5} \tag{8}$$

holds in the range of ϕ_p above $(\phi_p)_c$. Here, K' is a constant characteristic of the polymer + solvent system considered and $(\phi_p)_c$ denotes the value of ϕ_p at which $M_c(\phi_p)$ agrees with M_w, i.e.,

$$(\phi_p)_c = M_c^0/M_w \tag{9}$$

We introduce a function $g(T, \phi_p)$ defined by

$$g(T, \phi_p) \equiv \ln[\eta_p^0(T)\phi_p^{3.5}/\eta(T, \phi_p)] \tag{10}$$

where η_p^0 is the viscosity of the undiluted polymer. With equations (2), (5), and (8) substituted into equation (10), we obtain

$$g(T, \phi_p) = \frac{(1-\phi_p)[f_s(T, \phi_p) - f_p^0(T)]}{f_p^0(T)[f_p^0(T)\phi_p + f_s(T, \phi_p)(1-\phi_p)]} \tag{11}$$

which can be solved for $f_s(T, \phi_p)$ to give

$$f_s(T, \phi_p) = \frac{f_p^0(T)[1 - \phi_p + g(T, \phi_p)f_p^0(T)\phi_p]}{(1-\phi_p)[1 - g(T, \phi_p)f_p^0(T)]} \tag{12}$$

Hence, $f_s(T, \phi_p)$ can be evaluated from experimental information about $g(T, \phi_p)$ and $f_p^0(T)$. First, it is possible to compute g if data for $\eta(T, \phi_p)$ for known M_w and T are available up to $\phi_p = 1$. By the condition mentioned above, the data for $\phi_p < (\phi_p)_c$ should not be used for this computation. Next, equations (2) and (8) give

$$\eta_p^0(T) = K'M_w^{3.5}\exp[1/f_p^0(T)] \tag{13}$$

Thus, if the temperature dependence of $\eta_p^0(T)$ follows an equation of the Williams, Landel and Ferry (WLF) type[9], as is usually the case for amorphous polymers over the range $T_g^0 < T < T_g^0 + 100$(K) (where T_g^0 denotes the glass transition temperature for the undiluted polymer), $f_p^0(T)$ can be evaluated by the well known method[10] from data for η_p^0 as a function of T. For the polymers treated below, except for one, the values of α^0, T_g^0, and $f_p^0(T_g^0)$ in the expression

$$f_p^0(T) = f_p^0(T_g^0) + \alpha^0(T - T_g^0) \tag{14}$$

are available in the literature[10]. Hence, the necessary values of $f_p^0(T)$ for these polymers have been obtained by computation with equation (14).

Equation (2) gives $\zeta_p(T, 0) = A_p\exp[1/f_s^0(T)]$. Because $\zeta_p(T, 0)$ should be proportional to $\eta_s^0(T)$, the viscosity of the pure solvent, we have $\eta_s^0(T) \sim \exp[1/f_s^0(T)]$. Thus, if $\eta_s^0(T)$ varies with temperature in accordance with an equation of the WLF type (this is not always the case), $f_s^0(T)$ can be evaluated by the same method as that for $f_p^0(T)$.

DATA ANALYSIS

Poly(isobutylene) (PIB)

Tager *et al.*[11] reported accurate viscosity data for a PIB sample ($M_v = 1.2 \times 10^6$) in six solvents at 20°C over the entire range of composition. *Figures 1–4* show $f_s(20°\text{C}, \phi_p)$ and $f(20°\text{C}, \phi_p)$ as functions of ϕ_p computed from their data on four solvents: toluene, carbon tetrachloride, cyclohexane, and iso-octane. It was possible to evaluate $f_s^0(20°\text{C}, \phi_p)$ for the first three solvents, and the resulting values are indicated by double circles on the ordinate axes in *Figures 1, 2,* and *3*. The following features may be pointed out. In any of these four systems, $f_s(20°\text{C}, \phi_p)$ is either almost constant or increases slightly with decreasing ϕ_p, in the range

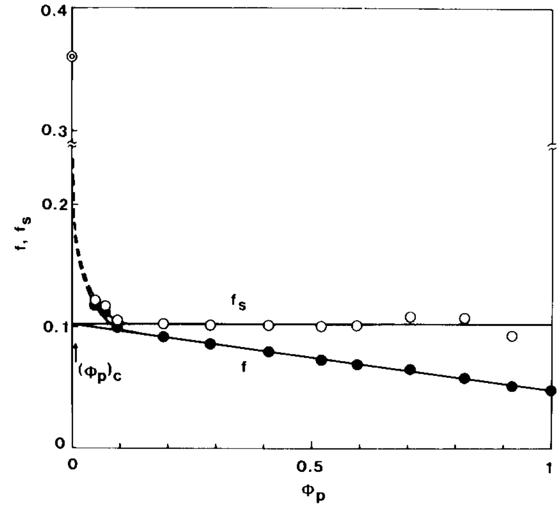

Figure 1 Concentration dependence of $f_s(T, \phi_p)$ (○) and $f(T, \phi_p)$ (●) for PIB + toluene at 20°C; $f_s^0(T)$ (◎) was computed from $f_s^0 = 0.36 + 1.7 \times 10^{-3}(T - 293.15)$ (T in K), derived by analysing the viscosity data in reference 18

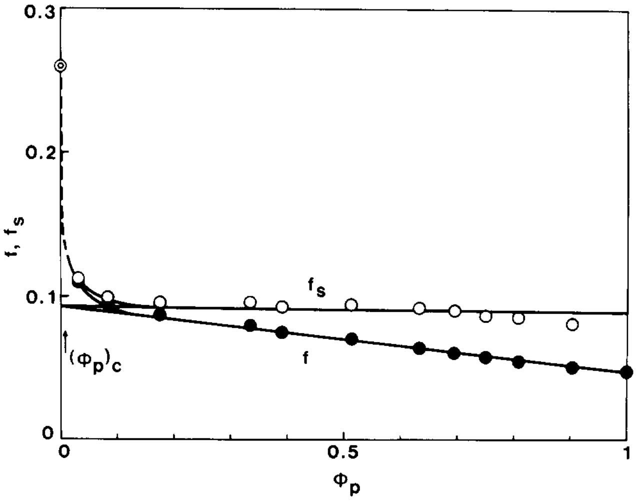

Figure 2 Concentration dependence of f_s (○) and f (●) for PIB + carbon tetrachloride at 20°C; f_s^0 was computed from $f_s^0 = 0.256 + 1.0 \times 10^{-3}(T - 291.41)$, derived by analysing the viscosity data in reference 19

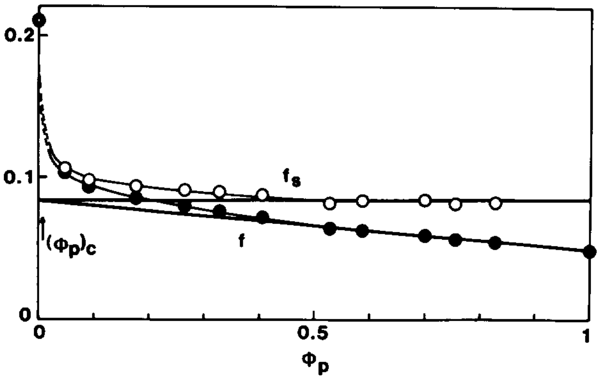

Figure 3 Concentration dependence of f_s (○) and f (●) for PIB+cyclohexane at 20°C; f_s^0 was computed from $f_s^0=0.217+7.9\times10^{-4}(T-293.15)$ (the data source is reference 18)

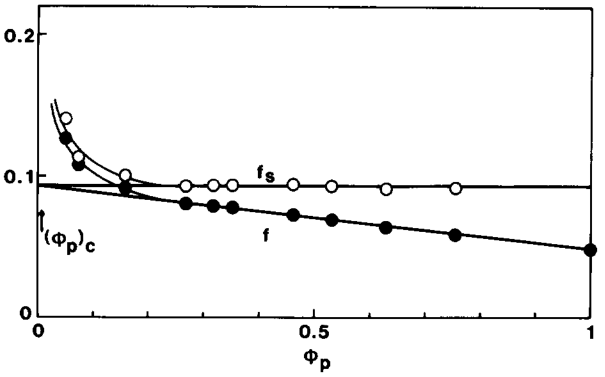

Figure 4 Concentration dependence of f_s (○) and f (●) for PIB+iso-octane at 20°C

$0.2<\phi_p<1$; $f(20°C, \phi_p)$ increases linearly with decreasing ϕ_p in the same concentration range. Both $f_s(20°C, \phi_p)$ and $f(20°C, \phi_p)$ swing sharply up as ϕ_p approaches $(\phi_p)_c$, which is found very close to $\phi_p=0$ for the high molecular weight PIB studied. In each figure, the line fitting the data points for $f_s(20°C, \phi_p)$ may be used to estimate $f_s(20°C, 1)$, which we denote by $f_s^*(20°C)$. For the toluene system we find $f_s^*(20°C)$ to be about 0.10. The value of $f_p^0(20°C)$ for PIB is computed by equation (14) to be 0.048. Hence, the ratio $\varepsilon(T)$ defined by

$$\varepsilon(T)=f_s^*(T)/f_p^0(T) \qquad (15)$$

is about 2 for the system PIB+toluene at 20°C. The values of $\varepsilon(20°C)$ for five other solvent systems were found to lie between 1.5 and 2.

The value of $f_s^0(20°C)/f_s^*(20°C)$ is 3.6, 3.2, and 2.5 for toluene, carbon tetrachloride, and cyclohexane, respectively. Because of the first feature mentioned these values are valid for $f_s^0(20°C)/f_s(20°C, \phi_p)$ in the range $0.2<\phi_p<1$. Thus, we can conclude that the fractional free volumes of toluene, carbon tetrachloride, and cyclohexane appreciably decrease when these solvents are trapped in entangled PIB.

Poly(methyl acrylate) (PMA)

Figure 5 shows $f_s(25°C, \phi_p)$ and $f(25°C, \phi_p)$ calculated from the viscosity data reported by Fujita and Maekawa[12], who obtained them with a sample of PMA ($M_v=1.3\times10^5$) in diethyl phthalate (DEP) over the entire range of composition at a series of temperature up to 100°C. The following features may be mentioned. $f_s(25°C, \phi_p)$ is almost constant until ϕ_p decreases to 0.70 and then gradually increases with lowering ϕ_p. Correspondingly, $f(25°C, \phi_p)$ increases linearly in the former region and somewhat more strongly in the latter region. The value of $\varepsilon(25°C)$ is 2.7. The value of $f_s^0(25°C)/f_s^*(25°C)$ is about 2.2, indicating that the fractional free volume of DEP in entangled PMA shrinks to about one half of that in the pure state.

Poly(alkyl methacrylate)

Okada[13,14] obtained extensive viscosity data for DEP solutions of poly(ethyl methacrylate) (PEMA; $M_v=8.8\times10^4$), poly(propyl methacrylate) (PPMA; $M_v=1.0\times10^5$), and poly(butyl methacrylate) (PBMA; $M_v=1.1\times10^5$) over the entire range of composition at a number of temperatures. *Figures 6*, *7*, and *8* illustrate $f_s(T, \phi_p)$ and $f(T, \phi_p)$ calculated from his data, with one temperature chosen for each polymer species. We see the following: for any of these polymers, $f_s(T, \phi_p)$ is constant and $f(T, \phi_p)$ depends linearly on ϕ_p in the range $(\phi_p)_c<\phi_p<1$; $\varepsilon(T)$ is 3.5 for PEMA (100°C), 2.7 for PPMA (80°C), and 2.7 for PBMA (80°C); $f_s^0(T)/f_s^*(T)$ is 2.7 for PEMA (100°C), 4.3 for PPMA (80°C), and 3.1 for PBMA (80°C).

As in PMA, the fractional free volumes of DEP in entangled PEMA, PPMA, and PBMA are significantly smaller than that in the pure state. No simple correlation can be seen between the free volume shrinkage and the side chain length.

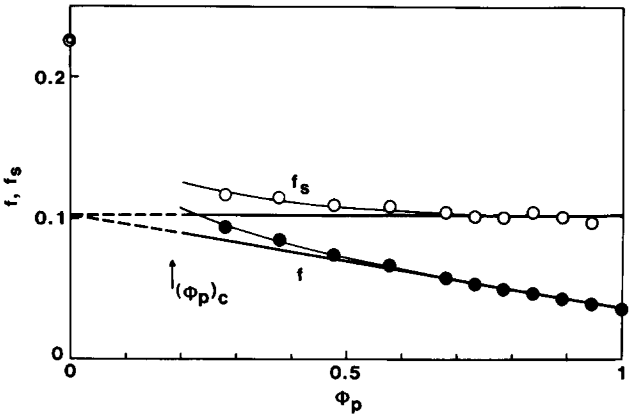

Figure 5 Concentration dependence of f_s (○) and f (●) for PMA+DEP at 25°C; f_s^0 was computed from $f_s^0=0.178+1.93\times10^{-3}(T-273.15)$ given by Okada[13]

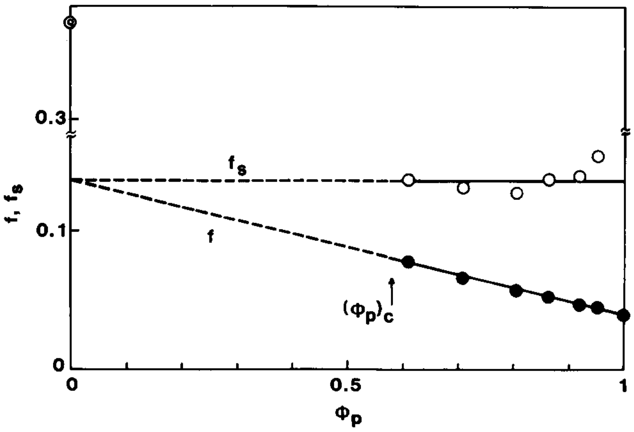

Figure 6 Concentration dependence of f_s (○) and f (●) for PEMA+DEP at 100°C

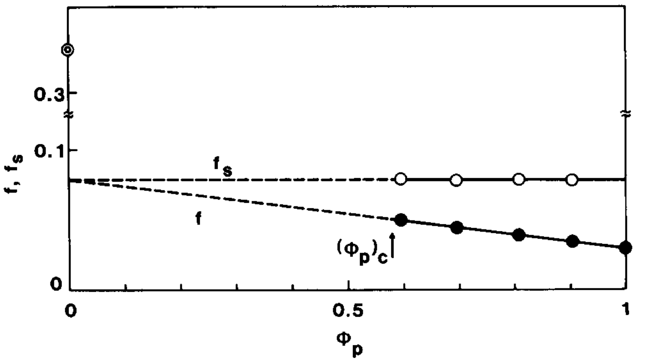

Figure 7 Concentration dependence of f_s (○) and f (●) for PPMA + DEP at 80°C

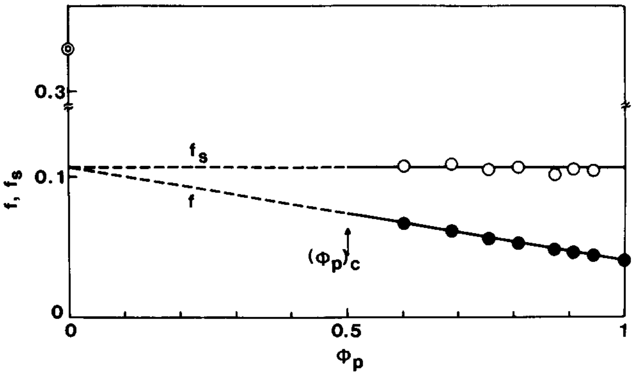

Figure 8 Concentration dependence of f_s (○) and f (●) for PBMA + DEP at 80°C

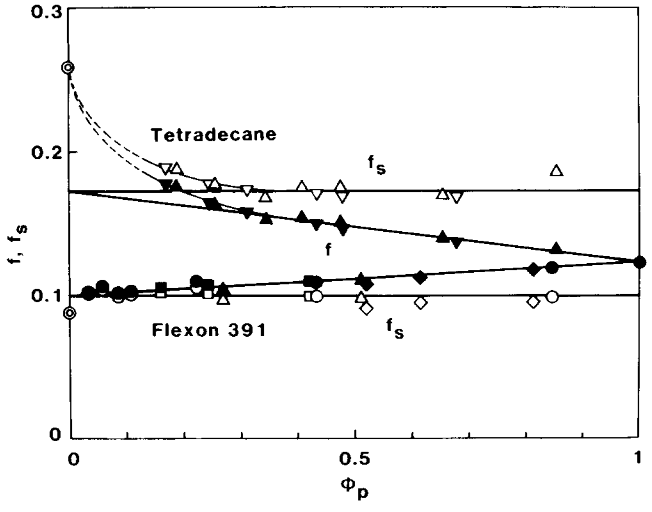

Figure 9 Concentration dependence of f_s (open symbols) and f (filled symbols) for PBD + tetradecane and PBD + Flexon 391 at 25°C. M_w is 3.5×10^5 (circles), 3.4×10^5 (triangles), 2.0×10^5 (squares), and 1.1×10^4 (lozenges); f_s^0 for tetradecane was calculated from $f_s^0 = 0.258 + 1.36 \times 10^{-3}(T - 298.15)$ (the data source is reference 19), and that for Flexon 391 from $f_s^0 = 1.03 \times 10^{-3}(T - 213.15)$ (the data source is reference 15)

Polybutadiene (PBD)

Marin *et al.*[15,16] reported viscosity data on tetradecane and Flexon 391 (an industrial oil) solutions of PBD at 25°C. *Figure 9* shows the results of our data analysis, which exhibit the following features. For either solvent, $f_s(25°\mathrm{C}, \phi_p)$ is essentially independent of ϕ_p, except at $\phi_p < 0.3$ for tetradecane, where f_s sharply swings up with decreasing ϕ_p. In *Figure 9*, different symbols refer to different values of M_w of the PBD samples, showing that f_s (and f_p^0) is independent of chain length, as would be expected. Although $(\phi_p)_c$ is not indicated here, the plotted points are all at ϕ_p above it for the respective PBD samples. ε(25°C) is 1.4 for tetradecane and 0.81 for Flexon 391. Interestingly, the latter figure is smaller than unity, differing from all the systems treated above. Thus, f(25°C) for Flexon 391 decreases linearly with decreasing ϕ_p, so that this solvent has an anti-plasticizing effect on the mobility of PBD. $f_s^0(25°\mathrm{C})/f_s^*(25°\mathrm{C})$ is 1.5 for tetradecane and 0.88 for Flexon 391. The latter figure implies that the fractional free volume of Flexon 391 expands in entangled PBD.

DISCUSSION

Inferences from data analysis

We may draw the following inferences or tentative conclusions on the behaviour of the fractional free volume in entangled solutions of amorphous polymers above T_g.

The fractional free volume of the solvent, $f_s(T, \phi_p)$, is little affected by polymer concentration, virtually maintaining its value at the limit $\phi_p \rightarrow 1$, i.e., f_s^* in the present notation. Hence, equation (5) can be approximated by

$$f(T, \phi_p) = f_p^0(T) + [f_s^*(T) - f_p^0(T)](1 - \phi_p) \quad (15)$$

Thus, equation (3) basic to the FK theory may be a good approximation to entangled polymer solutions if $\beta'(T)$ is interpreted as $f_s^*(T) - f_p^0(T)$.

$f_s^*(T)$ is not equal to the fractional free volume $f_s^0(T)$ of the solvent in the pure state, except for some special cases. The difference depends on polymer, solvent, and temperature, and, usually, $f_s^0(T)$ is larger than $f_s^*(T)$. Thus, $f_s^*(T)$ in equation (15) may not be replaced by $f_s^0(T)$. This means that equation (4) (the simple additivity in the fractional free volume) as assumed by Kelley and Bueche[2] is not adequate in general. The sharp change in $f_s(T, \phi_p)$ at low ϕ_p, as inferred from most of the graphs presented above, suggests that the solvent viscosity undergoes an appreciable effect from the coexisting polymer molecules in the dilute regime. What it implies will be a subject of considerable interest.

Model calculations

When equation (15) holds, it follows from equations (2) and (8) that

$$\frac{\eta(T\phi_p)}{\eta_p^0(T)} = (\phi_p)^{3.5} \exp\left\{ -\frac{(1 - \phi_p)(\varepsilon(T) - 1)}{f_p^0(T)[1 + (\varepsilon(T) - 1)(1 - \phi_p)]} \right\} \quad (16)$$

This equation shows that the temperature and concentration dependence of η/η_p^0 of entangled polymer solutions is governed by two parameters $f_p^0(T)$ and $\varepsilon(T)$. The former is characteristic of a given polymer species, while the latter is determined by the combination of polymer and solvent. Therefore, the solvent effect on the concentration dependence of η can be seen by changing $\varepsilon(T)$ over a range of practical interest, with $f_p^0(T)$ held constant. *Figures 10* and *11* illustrate the results of this operation for $f_p^0 = 0.10$ and 0.03, respectively. The chosen values of ε are in the range considered realistic from the above data analysis.

The curves in *Figure 10* are convex upward, except in the region of ϕ_p close to unity. According to Tager[17], this type of behaviour is generally observed in solutions of rubbery polymers, for which the choice $f_p^0 = 0.10$ is

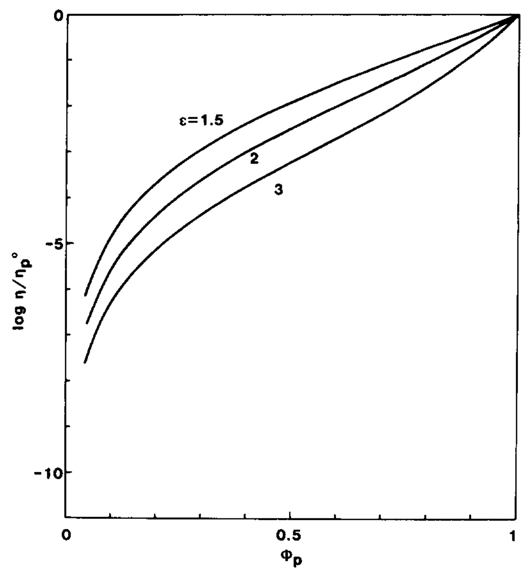

Figure 10 Calculated relations between η/η_p^0 for $f_p^0=0.10$ (typical of rubbery polymers) at the indicated values of ε

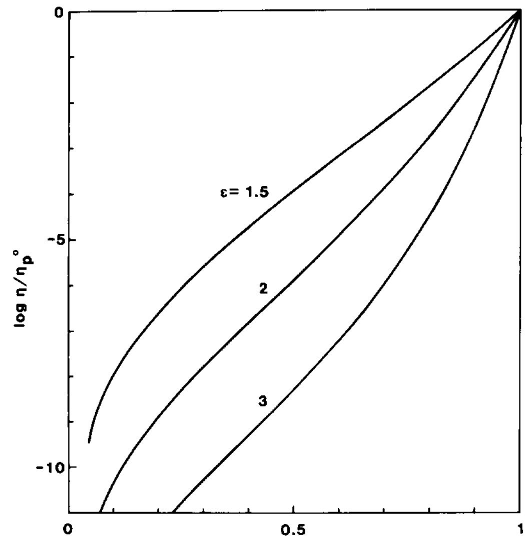

Figure 11 Calculated relations between η/η_p^0 for $f_p^0=0.03$ (typical of glassy polymers) at the indicated values of ε

relevant. On the other hand, $f_p^0=0.03$ corresponds to glassy polymers. *Figure 11* shows that unless ε is close to unity, the curves of $\log \eta$ *versus* ϕ_p for such polymers are concave upward over a wide range of high concentration. Tager[17] refers to this type of behaviour as characteristic of solutions of glassy polymers. Thus, we may expect that equation (16) explains the concentration dependence of η in entangled solutions of a variety of polymers.

When compared at the same ε, the curves in *Figure 11* are steeper than those in *Figure 10* at high concentrations, indicating that if ε is comparable, η in the entangled region increases more sharply with increasing ϕ_p as T is closer to T_g^0 so that f_p^0 is smaller.

Finally, we note that the curves depicted in *Figures 10* and *11* are meaningful only for $\phi_p > (\phi_p)_c$. Thus, for a polymer sample with $M_w \simeq 2M_c^0$, parts of them for $\phi_p < 0.5$ should be discarded.

CONCLUDING REMARKS

We analysed viscosity data on some polymer (rubbery and glassy) + solvent systems above the glass transition temperature on the basis of an empirical relation given by equation (5). The results showed that the solvent fractional free volume $f_s(T, \phi_p)$ in equation (5) is virtually constant over a broad range of concentration in which chain entanglement occurs. However, except for one system, the values of $f_s(T, \phi_p)$ were considerably smaller than f_s^0, the fractional free volume in the pure solvent. This finding implies that equation (4), i.e., the additivity in the free volume, may fail to describe the fractional free volume f of the solution in the entangled region.

Vrentas and Duda[6,7] have advocated the superiority of their free volume theory to the FK theory, but their argument is based on the misunderstanding that the FK theory uses equation (4) as its basis. What the FK theory assumed is not this equation but equation (3), with $\beta'(T)$ taken as an empirical function of temperature (it did not equate β' to $f_s^0 - f_p^0$). The present analysis has shown that equation (3) is a good approximation to entangled solutions and that β' is nearly equal to $f_s^* - f_p^0$, where f_s^* is the solvent fractional free volume at the limit $\phi_p \rightarrow 1$.

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