

Free Volume Treatment of Concentrated Polymer Solutions

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Synopsis

Very different concentration dependences of the viscosity of polymer solutions are predicted by the free volume treatments of Fujita and Kishimoto and of Kelly and Bueche. This latter is conveniently extended, and it is shown that it can describe a given set of experimental data over a concentration range much larger than the Fujita-Kishimoto equations.

Introduction

The concentration and temperature dependence of the viscosity of concentrated polymeric solutions has been recently interpreted on the basis of free volume considerations by Fujita and Kishimoto¹ and Kelley and Bueche.²

However, the equations derived by these authors are substantially different. The purpose of this paper is to examine these equations and to test their capacity of interpreting some experimental data within large ranges of the variables.

Treatment of Fujita and Kishimoto

Fujita and Kishimoto¹ (hereafter referred to as F-K) take the viscosity of a concentrated solution of "entangled" macromolecules having molecular weight M to be

$$\eta = k\phi_2 M^{3.4}\xi \quad (1)$$

where ϕ_2 is the volume fraction of polymer and ξ the friction coefficient of a monomeric unit in the chain.

They suggest that ξ depends on temperature and concentration through a Doolittle-type³ equation

$$\xi = A \exp \{1/F\} \quad (2)$$

where F is the total fractional free volume of the solution, given by

$$F = f_2 + \beta\phi_1 \quad (3)$$

f_2 being the fractional free volume of the pure polymer, β a parameter characteristic of the solvent, and ϕ_1 the volume fraction of solvent.

Following the suggestion of Ferry and Stratton⁴ and of Fujita⁵ the parameter β can be compared with the fractional free volume of the solvent, and can be written⁶

$$\beta = f_1 - f_2 \quad (4)$$

Equation (3) therefore becomes

$$F = f_1\phi_1 + f_2\phi_2 \quad (5)$$

which expresses the total free volume of the solution as the sum of the free volumes of polymer and solvent.

Combining the above equations, F-K obtain, for solutions of different volume fractions ϕ_1 and the reference state ϕ_1^*

$$-1/\ln (\eta\phi_2^*/\eta^*\phi_2) = F^* + [(F^*)^2/\beta(\phi_1 - \phi_1^*)] \quad (6)$$

which for the reference state $\phi_2^* = 1$ (pure polymer of viscosity η_0) gives

$$-1/\ln (\eta/\eta_0\phi_2) = f_2 + [(f_2)^2/\beta\phi_1] \quad (7)$$

Plotting the left side of eq. (6) or (7) against $(\phi_1 - \phi_1^*)^{-1}$ or ϕ^{-1} , F-K obtain the free volume parameters f_2 and β as function of temperature.

The values of f_1 so calculated range between 0.05 and 0.3, depending on the solvent and temperature.

The values of f_2 are found to be given by an experimental equation of the form

$$f_2 = f_g + \alpha(T - T_g) \quad (8)$$

where $f_g = 0.025$ is the well-known universal fractional free volume at the glass transition temperature T_g and α its expansion coefficient above T_g , which is of the order of 5×10^{-4} deg.⁻¹.

These results are in satisfactory agreement with the free volume fractions of polymers and solvents which can be expected from the Williams, Landel, and Ferry (WLF) equation.⁷

However, it has been found experimentally that the F-K equations can be applied only within quite narrow ranges of concentration, typically between the pure polymer of $\phi_2 = 0.8$.^{5,8,9}

It is known the WLF equation applies to pure polymers having fractional free volume less than 0.08, and Ferry and Stratton⁴ have supposed that a similar limitation should also hold for the concentrated solutions of polymers, so that the above F-K treatment should not be applicable to concentrations less than 0.8 by volume.⁴

Treatment of Kelley and Bueche

In the Kelley-Bueche (hereafter referred to as K-B) treatment² the viscosity of a solution of entangled macromolecules is given by

$$\eta = k\phi_2^4 M^{3.4}\xi \quad (9)$$

which, combined with eqs. (2) and (5) (assumption of the Doolittle equation for ξ and of the additivity of free volumes) gives

$$\ln (\eta/kM^{3.4}) = 4 \ln \phi_2 + (f_2\phi_2 + f_1\phi_1)^{-1} \quad (10)$$

The validity of the treatment is tested in the following way. The values of f_2 and f_1 are calculated, at constant temperature, from eq. (8), with the universal value of $f_g = 0.025$ and with an expansion coefficient α of approximately $5 \times 10^{-4} \text{ deg.}^{-1}$ for the polymer (as given by the WLF equation) and of the order of $10^{-3} \text{ deg.}^{-1}$ for the solvent.²

Insertion of f_2 and f_1 in eq. 10 gives $\ln (\eta/kM^{3.4})$ as a function of ϕ_2 . This "theoretical" curve is compared with the experimental $\ln \eta/\phi_2$ data by translation along the logarithmic axis. From the amount of translation the value of $kM^{3.4}$ can be calculated.

It was shown by Kelley-Bueche² and one of us¹⁰ that eq. (10) can be applied successfully to a variety of polymer-solvent systems, in large ranges of temperature and down to volume fractions ϕ_2 as low as 0.3. Also the molecular weight dependence predicted by eq. (10) was experimentally tested.¹⁰

With the reference state $\phi_2 = 1$, eq. (10) can be written

$$-1/\ln (\eta/\eta_0\phi_2^4) = f_2 + [(f_2)^2/(f_1 - f_2)\phi_1] \quad (11)$$

It may be seen that the F-K eq. (7) and the K-B eq. (11) differ by the additive term $\ln \phi_2^3$ on the denominator of the left side.

In the K-B treatment the fourth power of ϕ_2 in eq. (9) is derived from the Bueche¹¹ theory of the flow of entangled macromolecules.

For nonentangled macromolecules, both the Bueche¹¹ and the Rouse¹² theories of the flow of polymer solutions predict an equation of the form

$$\eta - \eta_s = k'\phi_2 M \xi \quad (12)$$

which, neglecting the viscosity of the solvent η_s , can be combined with eqs. (2) and (5) to give¹⁰

$$\ln (\eta/k'M) = \ln \phi_2 + (f_2\phi_2 + f_1\phi_1)^{-1} \quad (13)$$

It has been shown that this equation can be applied to relatively dilute polymer solutions and that the correct molecular weight and concentration dependence can be obtained.¹⁰

When the K-B eq. (13) for non-entangled solutions is written in the form of the F-K equations (taking the pure polymer as reference state) one obtains

$$-1/\ln (\eta/\eta_0\phi_2) = f_2 + [(f_2)^2/(f_1 - f_2)\phi_1] \quad (14)$$

which is exactly the F-K equation for entangled solutions.

Formulation of the Problem

The discrepancies between the above described treatments are the following.

(a) For entangled solutions the F-K and the K-B theories start from different initial equations and lead to final equations [eqs. (7) and (11)] which differ by the additive term $\ln \phi_2^3$ on the denominator of the left side.

(b) Fujita and co-workers^{1,5,8,9,13} apply their equation to several systems and find free volume parameters in good agreement with the values expected from the WLF equation. On the contrary K-B² and one of us¹⁰ insert the free volume parameters obtained from the WLF equation into the K-B eq. (10) and describe successfully several polymer solutions in wide concentration and molecular weight ranges.

(c) Furthermore, eq. 7 which F-K apply to entangled solutions is derived, following the K-B treatment, for non-entangled or dilute solutions, from an initial equation which has been shown indeed to be applicable to dilute polymeric systems.¹⁰

Results

The best way to solve the above contradictions is to examine with both theoretical treatments a given set of experimental data by using equations written in the same form, for example eqs. (7) and (11).

The extensive experimental data of Kishimoto¹³ on the system poly(vinyl acetate)-diethyl phthalate cover the complete range of concentrations at different temperatures and seem particularly suited for this purpose. For sake of clarity some of them are collected in Table I. The values of f_2 and f_1 for poly(vinyl acetate) and diethyl phthalate can be calculated from the f_g and α values reported by Ferry¹⁴ and by Garfield and Petrie⁶ and are reported in Table II.

In Figure 1 the data of Table I are plotted, following the F-K suggestion, as $-1/\ln(\eta/\eta_0\phi_2)$ against ϕ_1^{-1} . The values of f_2 and f_1 so obtained are

TABLE I
Viscosity ($\log \eta$) Data of Kishimoto on the System Poly(vinyl Acetate)-Diethyl Phthalate as a Function of Temperature and Polymer Concentration^a

ϕ_1 (20°C.)	ϕ_2 (20°C.)	$\log \eta$ at various temperatures					
		30°C.	40°C.	50°C.	60°C.	70°C.	80°C.
0.0	1.0	15.50	12.55	10.60	9.10	8.20	7.35
0.053	0.947	12.34	10.65	9.15	8.00	7.17	6.43
0.106	0.894	10.80	9.40	8.20	7.12	6.35	5.70
0.158	0.842	9.32	8.14	7.20	6.35	5.70	5.12
0.210	0.790	8.18	7.20	6.40	5.62	5.05	4.55
0.314	0.686	6.38	5.62	5.00	4.55	4.00	3.60
0.415	0.585	5.10	4.50	3.98	3.52	3.13	2.80
0.516	0.484	3.86	3.35	2.95	2.57	2.28	2.02
0.615	0.385	2.88	2.52	2.20	1.85	1.62	1.42
0.714	0.286	2.04	1.73	1.44	1.24	1.06	0.90
0.811	0.189	1.37	0.957	0.746	0.536	0.45	0.25

^a The densities and volume fractions at temperatures different than 20°C. have been computed by assuming no volume changes in mixing from the values at 20°C. and the expansion coefficients given by Kishimoto.¹³

TABLE II
Free Volume Parameters for Poly(vinyl Acetate) (f_2) and Diethyl Phthalate (f_1) between 30 and 80°C.

Temperature, °C.	Calculated from WLF equation ^a		From Fig. 1 [eq. (7)]		From Fig. 2 [eq. (15)]		From Fig. 2 [eq. (16)]	
	f_2	f_1	f_2	f_1	f_2	f_1	f_2	f_1
30	0.027	0.119	0.025	0.06	0.027	0.136	0.028	0.139
40	0.033	0.127	0.029	0.107	0.032	0.131	0.033	0.132
50	0.039	0.136	0.031	0.094	0.037	0.128	0.039	0.136
60	0.044	0.144	0.038	0.11	0.041	0.127	0.044	0.137
80	0.056	0.160	0.052	0.17	0.053	0.175	0.056	0.174

^a For the polymer, $f_g = 0.028$, $\alpha = 5.9 \times 10^{-4}$ deg.⁻¹, $T_g = 32^\circ\text{C}$.; for the solvent, $f_g = 0.025$, $\alpha = 8.2 \times 10^{-4}$ deg.⁻¹, $T_g = -85^\circ\text{C}$.

shown in Table II. It may be noted that the straight lines of Figure 1 (which corresponds to Figure 9 of the original paper¹³) describe the experimental data only from the pure polymer to $\phi_2 = 0.7$. At lower concentrations there is a deviation with a downward curvature, which has been reported^{1,8,13} as a general feature of this kind of plot. In Figure 1 the range of

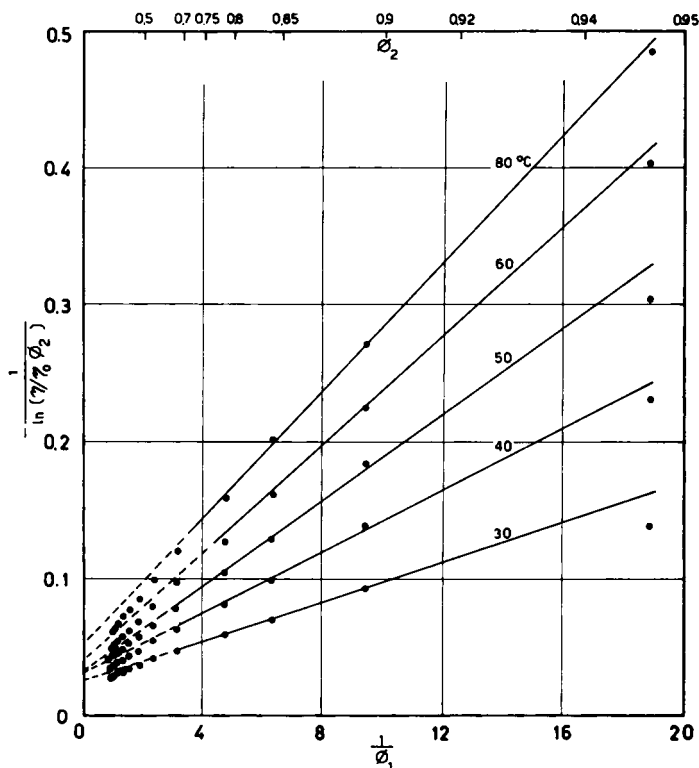


Fig. 1. Solutions of poly(vinyl acetate) and diethyl phthalate. Data of Table I¹³ plotted according to the Fujita-Kishimoto equation [eq. (7)].

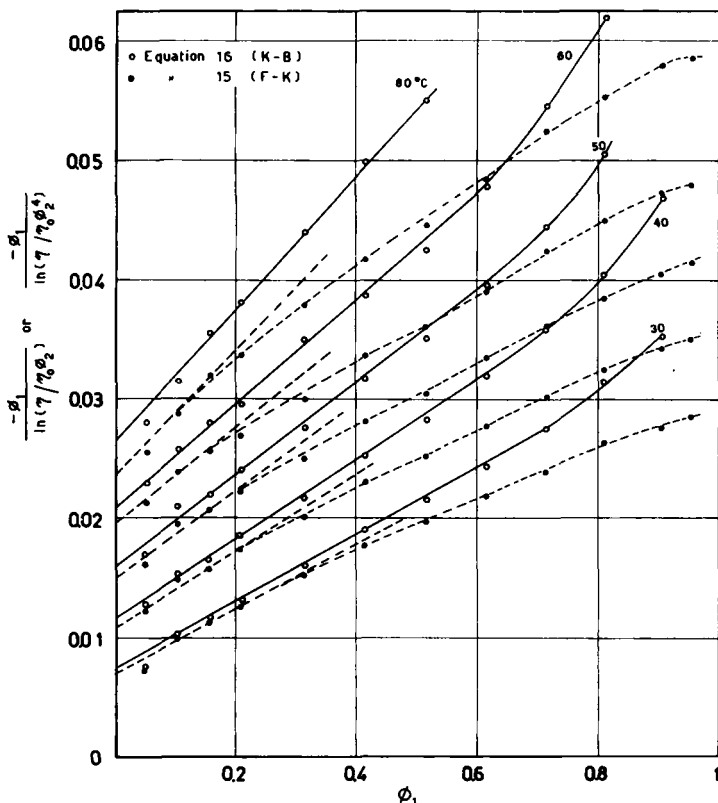


Fig. 2. Plot of the data of Table I according to the eqs. (15) and (16).

ϕ_2 from 0.7 to zero is abnormally restricted, and the experimental data are crowded, due to the fact that ϕ_1^{-1} is used as abscissa. A more adequate way of plotting the viscosity-concentration data can be the following⁵: eq. (7) is rearranged and written

$$-\phi_1 / \ln (\eta / \eta_0 \phi_2) = [(f_2)^2 / (f_1 - f_2)] + f_2 \phi_1 \quad (15)$$

and its left side is plotted against ϕ_1 . Analogously, the K-B equation (15) becomes

$$-\phi_1 / \ln (\eta / \eta_0 \phi_2^4) = [(f_2)^2 / (f_1 - f_2)] + f_2 \phi_1 \quad (16)$$

The plots become therefore linear with respect to ϕ_1 and their slopes give the free volume fraction of polymer f_2 .

The data of Table I are plotted accordingly in Figure 2.

It is seen that the K-B eq. (16) gives straight lines up to ϕ_1 of the order of 0.6 (ϕ_2 between 1 and 0.4) while the experimental data deviate from eq. (15) when ϕ_1 is larger than approximately 0.2 (ϕ_2 smaller than 0.8).

Also, the free volume fractions f_2 and f_1 obtained from eq. (16) can be compared with those calculated from the WLF values^{6,14} better than the

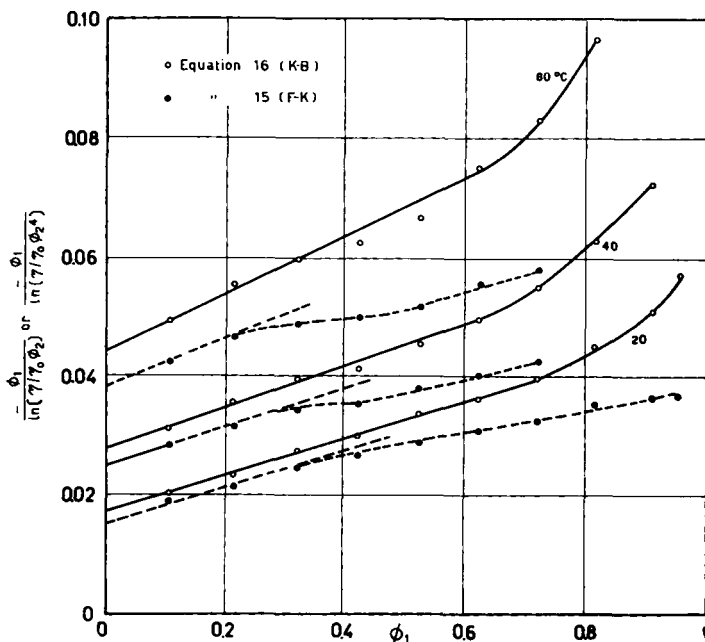


Fig. 3. Solutions of poly(methyl acrylate) and diethyl phthalate. Data taken from Fujita and Maekawa⁸ and plotted according to eqs. (15) and (16).

parameters obtained from either eq. 15 or eq. (7) (Figure 1), as can be seen from Table II.

This analysis clearly shows that the K-B treatment gives a more adequate representation of the data of Table II than the equations derived from the F-K treatment.

The data of Fujita and Maekawa⁸ on the system poly(methyl acrylate)-diethyl phthalate can give a further confirmation of the above findings.

Some viscosity values read from their graph are plotted in Figure 3.

It is seen that eq. 15 fails to describe the data above $\phi_1 = 0.3$, while eq. (16) is applicable up to $\phi_1 = 0.6$.

Several other systems examined in the course of this work gave similar results.

Discussion

Both the theories discussed above are derived from the iso-free volume concept of the glass transition temperature and from the Doolittle equation.

In the original treatment of Kelley and Bueche² the assumption of additivity of free volumes of polymer and diluent is made, while in the F-K treatment, and in the elaboration of the K-B treatment presented in this paper [eqs. (11) and (16)] the assumption of additivity, strictly speaking, is not necessary, because only the linear dependence of F on ϕ_1 [eq. (3)] is required.

The difference between the two theories does not involve the concentration dependence of the friction coefficient ξ , but only the fourth power dependence of η on concentration.

The fourth power of ϕ_2 in the equation of K-B is directly derived from the original Bueche theory¹⁵ of the flow of entangled systems, as a consequence of the proportionality of the critical molecular weight between entanglements M_c and the reciprocal polymer concentration¹⁶

$$M_c = K/\phi_2 \quad (17)$$

As shown in Figures 2 and 3, eq. (16) derived from the K-B treatment for entangled solutions, seems more adequate than the F-K equations to describe the experimental data in large ranges of concentration. This result of course supports the K-B treatment and its previous applications.^{2,10}

It remains to be explained why Fujita and co-workers^{1,5,9} obtain reasonable values of f_2 and f_1 from their equations.

It is seen from Figure 1 that in the F-K plots the slope and intercept of the straight lines [eq. (7)] are determined by the viscosity of a narrow range of concentration near the pure polymer. From Figures 2 and 3 it is clear that for $\phi_1 < 0.2$ the two series of curves can be drawn with approximately the same slope.

In this concentration range the values of $\ln \phi_2^4$ and of $\ln \phi_2$ can be rather close. For example, at $\phi_2 = 0.8$ they differ by 0.67 units, which is small compared with $\ln (\eta_0/\eta)$ if this latter is of the order of 10.

In fact, at temperatures not too far from the polymer glass transition temperature, the addition of 20% by volume of diluent to the polymer can lower the viscosity of a factor between 10^7 and 10^2 (see Table I), so that the value of $\ln (\eta_0/\eta)$ is between 16 and 4.6. Under these conditions ($\phi_2 > 0.8$) eqs. (15) and (16) do not differ very much.

It is therefore understandable that the Fujita-Kishimoto treatment gives, in some instances, values of the free volume parameters which agree with those expected from the WLF equation and with those obtained from the application of the "correct" eq. (15).

As shown in the present paper, this latter can be considered a useful extension of the K-B treatment, since it allows precise determination of f_2 and f_1 to be carried out from the knowledge of the concentration dependence of the viscosity of polymeric solutions.

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Résumé

On prévoit des dépendances très différentes de la concentration en ce qui concerne la viscosité de solutions polymériques en se basant sur les traitements de volume libre de Fujita-Kishimoto et de Kelley-Bueche. Cette dernière méthode peut être avantageusement élargie et on montre qu'elle permet de décrire un ensemble de données expérimentales sur un domaine de concentration beaucoup plus vaste que les équations de Fujita-Kishimoto.

Zusammenfassung

Die Theorien des freien Volumens von Fujita-Kishimoto und von Kelley-Bueche lassen sehr verschiedenartige Typen der Konzentrationsabhängigkeit der Viskosität von Polymerlösungen erwarten. Die zweitgenannte Behandlungsweise kann bequem erweitert werden und es wird gezeigt, dass damit eine gegebene Reihe von Versuchsdaten über einen viel grösseren Konzentrationsbereich beschrieben werden kann als mit den Gleichungen von Fujita-Kishimoto.

Received April 28, 1966

Prod. No. 1403