

## Viscosity of Concentrated Polymer Solutions. II. Application of a Free-Volume Treatment to Solutions of Poly(vinyl Chloride) in Cyclohexanone and to Other Polymer Solutions

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### Synopsis

The Kelley-Bueche free-volume treatment of the viscosity of polymeric solutions has been applied to the previously reported data on poly(vinyl chloride)-cyclohexanone solutions and to several other polymer-diluent systems. It has been shown that the theoretical equations, based on the assumption of the additivity of free volumes of the components, are capable of predicting with remarkable accuracy the concentration, temperature, and molecular weight dependence of the viscosity of the investigated solutions over very large ranges of the variables.

### INTRODUCTION

In a previous paper<sup>1</sup> a number of data on the concentration and molecular weight dependence of the viscosity of poly(vinyl chloride) (PVC) in cyclohexanone were reported. It was shown that the description of this system as well as of other polymer solutions by means of empirical equations cannot give satisfactory results over broad ranges of the variables.

A theoretical treatment of the viscosity of polymer solutions, based both on the Bueche model of flow for undiluted polymers and on the free-volume concept, has been presented recently by Kelley and Bueche.<sup>2</sup> This paper discusses the extension and application of the Kelley-Bueche treatment to changes of concentration and molecular weight for the system PVC-cyclohexanone as well as for other polymer-diluent pairs for which data are available over broad ranges of concentration, molecular weight, and temperature.

### FREE VOLUME REPRESENTATION

A number of theories have been proposed to interpret the viscosity of simple liquids.<sup>3</sup> The equations concerning the macroscopic behavior of liquids are usually derived from considerations on microscopic models, and the theories more widely applied are based on the concept of a liquid structure which is assumed to be actually full of cavities or holes.<sup>4-6</sup>

They constitute an extra volume or "free volume"  $v_f$  which has been defined as the excess of the specific volume of the liquid  $v$  over that of the corresponding glass at absolute zero  $v_0$ :

$$v_f = v - v_0 \quad (1)$$

Assuming that the molecular motions are permitted only if a free volume is available, the liquid fluidity should increase with  $v_f$ , as suggested by Batschinski.<sup>7</sup>

The equation relating the viscosity to the free volume, first given by Doolittle,<sup>8</sup> has been derived theoretically by Bueche<sup>9</sup> and Cohen and Turnbull<sup>10</sup> on the basis of a liquid model of hard spheres within which there is a statistical redistribution of the free volume:

$$\ln \eta = A + (b/f) \quad (2)$$

where  $b$  is a constant of the order of unity and  $f$  is the fractional free volume,  $f = v_f/v$ .

The effect of the temperature on viscosity is primarily due to the increase in free volume resulting from the thermal expansion of the liquid. For glass-forming liquids above their glass transition temperature  $T_g$ , it is generally assumed that the fractional free volume is given by:

$$f = f_g + \alpha_f(T - T_g) \quad (3)$$

where  $f_g$  is the fractional free volume at  $T_g$  and  $\alpha_f$ , the expansion coefficient of free volume, is approximately given by the difference between the expansion coefficient of the liquid  $\alpha_l$  and of the glass  $\alpha_g$ :

$$\alpha_f \cong \alpha_l - \alpha_g \quad (4)$$

On combining eqs. (2) and (3), written at temperatures  $T$  and  $T_g$ , the well-known equation of Williams-Landel-Ferry (WLF)<sup>11</sup> can be derived:

$$\ln (\eta/\eta_{T_g}) = -b(T - T_g)/f_g[(f_g/\alpha_f) + T - T_g] \quad (5)$$

Equation (5) applies to numerous liquids, both simple and polymeric,<sup>11-14</sup> with a value near unity for  $b$  and the "universal" average values of 0.025 for  $f_g$  and of  $4.8 \times 10^{-4}$  deg.<sup>-1</sup> for  $\alpha_f$ .

For polymers in the rubbery or molten state, the WLF equation describes the effect of the temperature on the viscosity, while the effect of the molecular weight on  $\eta$  is given by the empirical equation

$$\eta = K^\dagger M^{a'} \quad (6)$$

where  $K^\dagger$  is a constant at constant temperature and  $a'$  has the value of 3.4 above some critical molecular weight  $M_c$ , while below  $M_c$   $a'$  is of the order of unity.<sup>15</sup>

The transition from the low-power dependence to the 3.4-power dependence at the critical molecular weight has been interpreted by Bueche<sup>16</sup> on the basis of a molecular flow model, valid for any polymeric system, in which the macromolecules form a transient network structure through

chain entanglements. The formation of such entanglements, of course, requires sufficient length and concentration of the macromolecules. When the number of entanglements is below some critical value (less than two per molecule), the polymer network cannot exist, and the polymer chains in motion are subjected to a viscous resistance proportional to their dimension, as in dilute solution. The viscosity is given by

$$\eta = k'CM\xi_0 \quad (7)$$

where  $C$  is the concentration,  $M$  the molecular weight of the polymer, and  $\xi_0$  is the "segmental friction factor," proportional to the local, or microscopic, viscosity encountered by the molecular segments in their motion.<sup>16</sup> Equation (7) is substantially similar to the equation derived, in the molecular theory of Rouse,<sup>17</sup> for dilute solutions of macromolecules:

$$\eta - \eta_s = (N a^2/36 M_0^2)CM \zeta_0 \quad (8)$$

where  $\eta_s$  is the solvent viscosity,  $N$  Avogadro's number,  $M_0$  the monomer molecular weight,  $\zeta_0$  the monomeric friction factor, and  $a$  is defined by the relation:

$$a^2 = M_0(\bar{r}^2/M) \quad (9)$$

$(\bar{r}^2)^{0.5}$  being the root-mean-square end-to-end length of the entire macromolecular chain in solution.<sup>18</sup>

Above the critical concentration of chain entanglements, a molecule in motion is retarded by them, and following the Bueche model this results in a viscosity proportional to the 3.5 power of molecular weight. A more detailed form of eq. (6), as given by Bueche, is the following:

$$\eta = kC^4M^{3.5}\xi_0 \quad (10)$$

The viscometric properties of polymer solutions can be given by eqs. (7) and (10) if the concentration and temperature dependence of  $\xi_0$  is known. To describe it, Kelley and Bueche<sup>2</sup> take the fraction factor  $\xi_0$  to be a function of the free volume fraction  $f$  alone, as given by eq. (2) if  $\eta$  is substituted by  $\xi_0$ , and assume that the fractional free volumes of the polymer  $f_2$  and of the solvent  $f_1$  are strictly additive in solution, so that the total fractional free volume in the system is given by

$$F = \phi_2 f_2 + (1 - \phi_2) f_1 \quad (11)$$

where  $\phi_2$  is the volume fraction of the polymer in the solution. Equations (2), (10), and (11) can be combined to give:

$$\ln(\eta/B) = 4 \ln C + [\phi_2 f_2 + (1 - \phi_2) f_1]^{-1} \quad (12)$$

where  $B = KM^{3.5}$ , with the constant  $K$  resulting from the grouping of the various constants of the above-written equations.

Since the free volume fractions  $f_2$  and  $f_1$  are given by eq. (3) as functions of the glass transition temperatures and of the expansion coefficients of polymer and solvent, eq. (12) should describe the effect of temperature,

concentration, and molecular weight on the viscosity of polymer solutions with the aid of only one adjustable parameter,  $K$ . Kelley and Bueche have shown that it could be applied to three different polymer-solvent systems in relatively large ranges of concentration and at different temperatures. The dependence of  $B$  on molecular weight was not explored in their work.

Moreover, it must be noted that eq. (12) applies only to solutions in which the molecules participate in an entangled network of macromolecular chains. At low concentrations and/or low molecular weight the network cannot exist, the molecules being separated from each other or too short to entangle. In these conditions, an extension of the Kelley-Bueche treatment leads, from eqs. (2), (7), and (11), to the relation:

$$\ln(\eta/B') = \ln C + [\phi_2 f_2 + (1 - \phi_2) f_1]^{-1} \quad (13)$$

where  $B' = K'M$ .

Equations (12) and (13) should predict the viscosity of polymer-solvent systems above their glass transition temperatures over the entire range of concentration and for any molecular weight. At constant molecular weight and temperature, eq. (13) should apply below, and eq. (12) above a critical concentration  $C^*$ , where the two curves  $\eta/C$  cross each other (and above which chain entanglements form).

## COMPARISON WITH EXPERIMENTAL DATA

### Poly (vinyl Chloride)-Cyclohexanone

The application of eqs. (12) and (13) to the results presented previously<sup>1</sup> on PVC-cyclohexanone solutions requires the knowledge of the fractional free volumes  $f_2$  and  $f_1$  of polymer and solvent at 30°C. As this temperature is below the glass transition temperature of the polymer, reported as 82°C. by several authors,<sup>13,19-21</sup> the value of  $f_2$  at 30°C. can either be considered constant (for any temperature  $T \leq T_g$ ) and equal to  $f_g$ <sup>18</sup> or calculated, even at  $T < T_g$ , by means of eq. (3). In this work it has been found that the second method gives better results, as will be shown later for a different solvent-polymer system.

However, it must be noted that eq. 3 gives absurd (negative) values of  $f_2$  for temperatures lower than  $T_0 = T_g - (f_g/\alpha_f)$ . This presumably was the case for the polystyrene-diethylbenzene solutions at 30°C. reported by Kelley and Bueche.<sup>2</sup> Therefore it must be stated that eq. (3) can be used only for positive values of  $f_2$ , while for temperatures lower than  $T_0$  the value of  $f_2$  is zero.<sup>13</sup>

For PVC the expansion coefficient of free volume  $\alpha_f$ , as calculated from the application of the WLF equation to dielectric relaxation processes,<sup>14</sup> is  $5.0 \times 10^{-4}$  deg.<sup>-1</sup>, which agrees well with the difference  $\alpha_i - \alpha_g$  obtained from volumetric measurements ( $4.8 \times 10^{-4}$  deg.<sup>-1</sup>).<sup>13</sup> Inserting this value in eq. (3) gives a free volume fraction  $f_2$  at 30°C. which is practically zero.

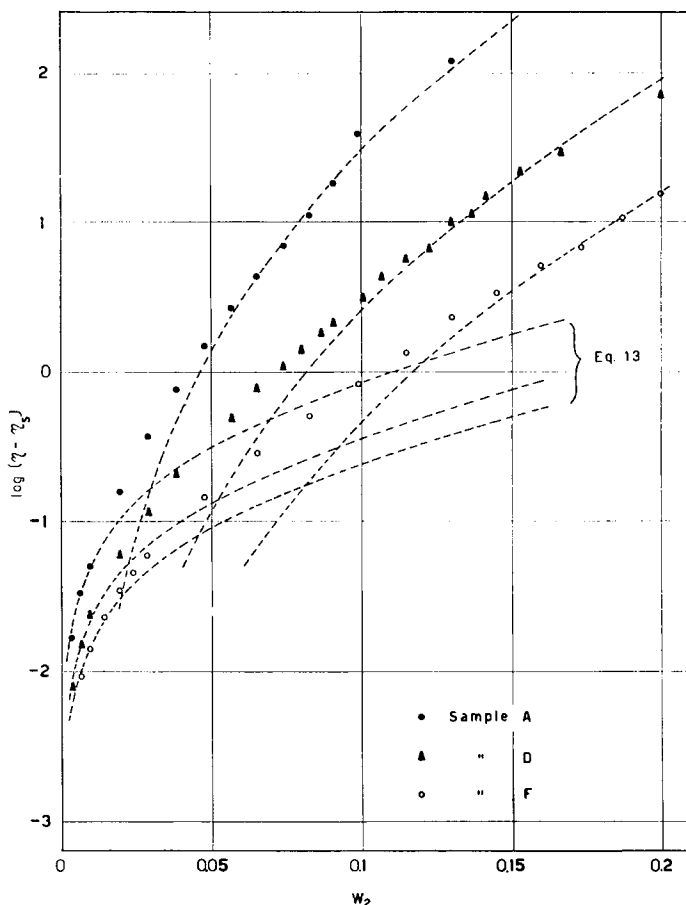


Fig. 1. Logarithm of  $(\eta - \eta_2)$  plotted against the polymer weight fraction  $w_2$  for the PVC samples A, D, and F: (---) theoretical eqs. (12) and (13) at 30°C.; (●▲○) experimental data from reference 1.

The value of  $f_1$  at 30°C. can be evaluated in the following way. Since the experimental  $T_g$  for cyclohexanone is unknown, it may be calculated by the approximate relation  $T_g \cong 0.65 T_m$ , where  $T_m$  is the melting temperature.<sup>22,23</sup> The resultant  $T_g$  is -120°C., close to the value experimentally determined for cyclohexanol and for a number of alcohols and glycols.<sup>24</sup> The thermal expansion coefficient of cyclohexanone has been determined as  $9.2 \times 10^{-4} \text{ deg.}^{-1}$  at room temperature.<sup>1</sup> Taking the expansion coefficient of the glass approximately as  $10^{-4} \text{ deg.}^{-1}$ , the value of  $8 \times 10^{-4} \text{ deg.}^{-1}$  can be used as the  $\alpha_f$  of cyclohexanone. The resultant free volume fraction  $f_1$  at 30°C. is 0.145. Insertion of  $f_2$  and  $f_1$  in eqs. (12) and (13) gives  $\ln(\eta/B)$  and  $\ln(\eta/B')$  as a function of concentration. This can be expressed as weight fraction  $w_2$ , calculated from  $\phi_2$  by assuming the volumes of solvent and polymer to be additive. The theoretical viscosity-

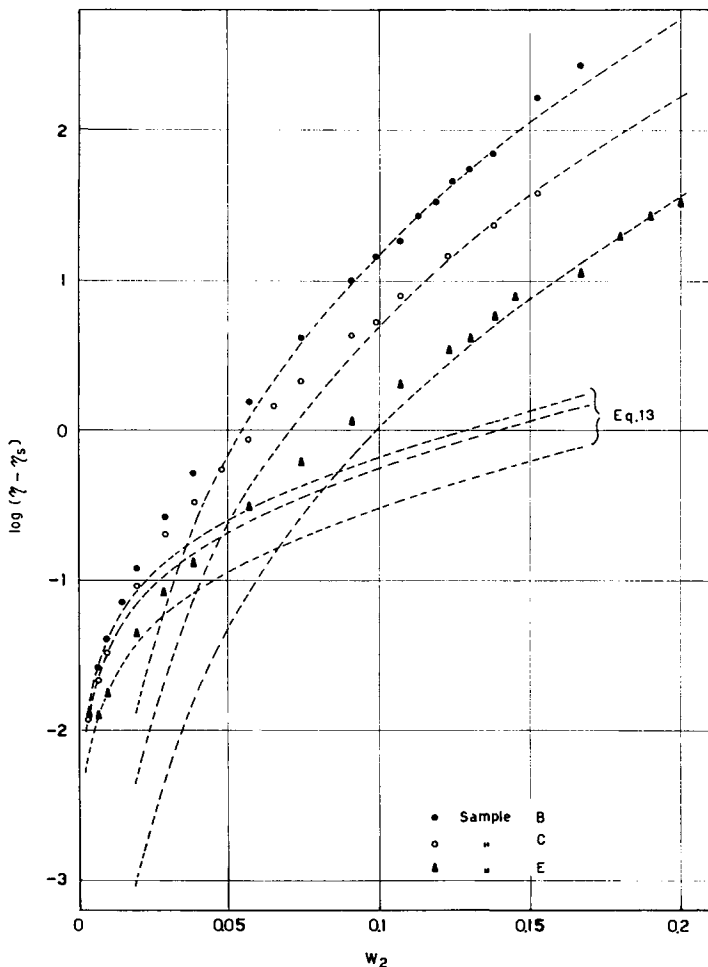


Fig. 2. Logarithm of  $(\eta - \eta_s)$  plotted against  $w_2$  for the PVC samples B, C, and E. Key to figure same as in Fig. 1.

concentration curves as thus obtained are compared with the experimental results in Figures 1-3. Following eq. (8), the viscosity of solvent has been subtracted from the solution viscosity in the experimental data.

Superposition with the theoretical curves has been achieved by vertical translation along the logarithmic viscosity axis. The amount of translation gives the values of the adjustable parameters  $B$  and  $B'$ , which are collected in Table I.

It may be seen from Figures 1-3 that for the polymers having high molecular weight the eq. (13) (which should be valid for nonentangled solutions) can be superposed to the experimental data only over a narrow range of concentrations, from  $w_2 = 0.003$  to  $w_2 = 0.01$ , while for the low molecular weight sample H the same equation can be applied successfully up to

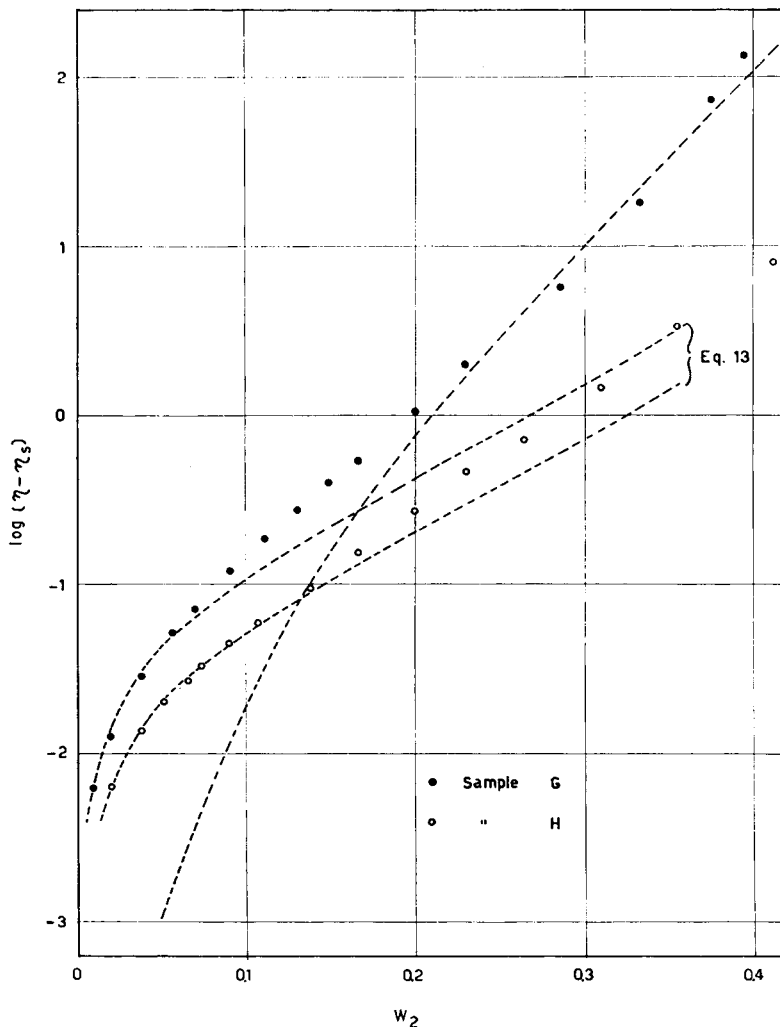


Fig. 3. Logarithm of  $(\eta - \eta_s)$  plotted against  $w_2$  for the PVC samples G and H. Key to figure same as in Fig. 1.

the weight fraction 0.16. On the contrary, eq. (12) (valid for entangled solutions) describes well the experimental data for samples of high molecular weight above weight fractions of the order of 0.05, whereas it cannot be applied to samples H at a  $w_2$  lower than 0.4. The applicability of both the equations is therefore determined by the molecular weight and the concentration of the solution. As may be seen in Figures 1-3, the main characteristics of the concentration dependence of the viscosity of PVC-cyclohexanone solutions is described satisfactorily by the Kelley-Bueche treatment. Moreover, it can be shown that also the molecular weight dependence of viscosity is correctly predicted by it. In fact, when the

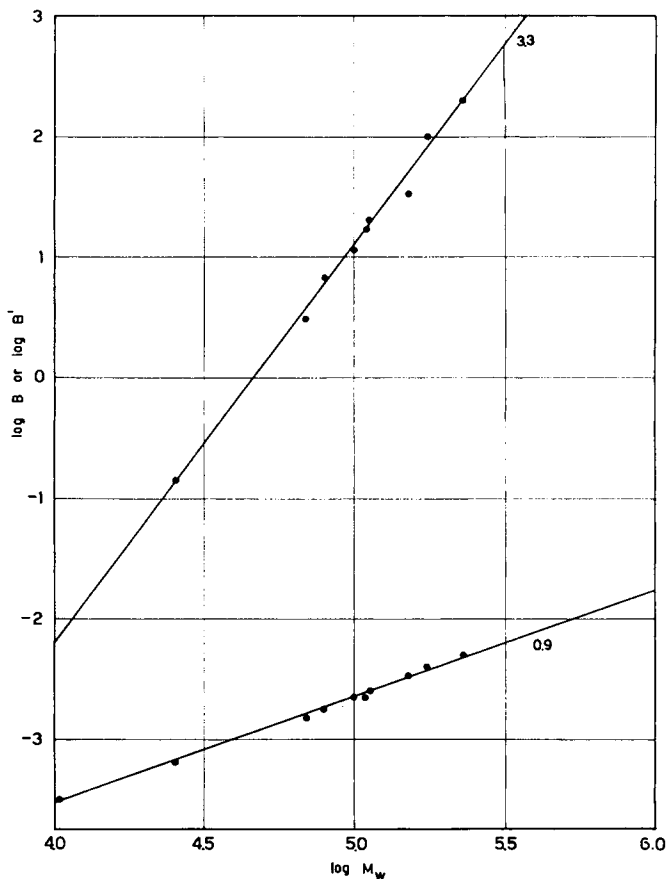


Fig. 4.  $\log B$  and  $\log B'$ , as derived from Figs. 1-3, plotted against the logarithm of the molecular weight  $M_w$  of the PVC samples of Table I.

TABLE I  
Values of the Parameters  $B$ ,  $B'$  and  $K_z$ ,  $K_z'$  (see Text) for PVC-cyclohexanone Solutions at 30°C.

PVC sample	$\overline{M}_w \times 10^{-3}$	$\log B$	$\log B'$	$\log K_z$	$\log K_z'$
A	230	2.30	-2.30	-11.2	-6.2
B	174	2.00	-2.39	-11.1	-6.1
C	151	1.52	-2.48	-11.4	-6.2
D	110	1.23	-2.66	-11.2	-6.2
E	80	0.84	-2.74	-11.1	-6.1
F	70	0.49	-2.83	-11.2	-6.2
G	26	-0.85	-3.20	-11.1	-6.1
H	10.5	—	-3.50	—	-6.0
I	100	1.33	-2.62	-10.9	-6.1
L	112	1.04	-2.66	-11.4	-6.2



parameters  $B$  and  $B'$  are plotted on log-log paper against the weight-average molecular weight of the polymers  $M_w$ , two straight lines are obtained (Fig. 4). Their slopes are 3.3 and 0.9, respectively, in close agreement with the theoretical slopes 3.5 and 1.0 required by eqs. (12) and (13).

There is, however, a notable discrepancy between theoretical curves and experimental data, since these latter show no sign of a sudden change in the slopes of the  $\log(\eta - \eta_s)$  versus  $w_2$  curves plotted in Figures 1-3 while the theoretical curves cross, at a given critical concentration  $C^*$ , with very different slopes. In a relatively large range centered around  $C^*$ , therefore, the experimental data differ consistently from the predicted theoretical curves. As noted previously,<sup>1</sup> in literature there is no evidence of a transition in the slopes of the  $\log \eta - w_2$  curves for polymer-solvent systems, and it will be shown later that the discrepancy of Figures 1-3 will be confirmed by the data of other authors, as discussed below.

### APPLICATION TO OTHER POLYMER SOLUTIONS

The application of eqs. (12) and (13) to viscometric data on polymer solutions reported in the literature requires only the knowledge of the glass transition temperatures and of the expansion coefficients of polymers and solvents. These values are usually known or can be estimated with reasonable accuracy.

Unless otherwise indicated, the value of  $f_g = 0.025$  was used in these comparisons, while the numerical value of  $\alpha_f$  for some systems was found in the literature and for other systems was estimated from the thermal expansion coefficients through eq. (4). For temperatures lower than the  $T_g$  of the polymers, the value of  $f_2$  was calculated from eq. (3).

Some of the available viscometric data have been reviewed, and their characteristics are summarized in Table II.

The theoretical curves calculated from eq. 12 are superposed to the experimental data by using the procedure described above. In some cases the curves given by eq. (13) have also been calculated.

#### Polyisobutylene-Isooctane

Figure 5 shows the results obtained from the data of Tager et al.<sup>25</sup> on the system polyisobutylene-isooctane at 20°C. Five samples having molecular weights from 900 to  $1.2 \times 10^6$  were explored. The values of  $\eta$  at various  $\phi_2$  are compared with the theoretical curves calculated by using the data of Table II. It may be seen that eq. (12) can be applied with excellent results in the range of  $\phi_2$  from 0.1 to 1 for all samples except for that having the lowest molecular weight. The values of  $\log B$ , when plotted versus  $\log M$ , give a straight line with slope 3.3, which agrees well with the theoretical value of 3.5 (see Fig. 6).

#### Poly(decamethylene Adipate)-Diethyl Succinate

The application of eqs. (12) and (13) to Flory's data on this system<sup>26</sup> is seen in Figure 7. The value of  $f_g$  was taken as 0.035 for this polymer.<sup>27</sup>

TABLE II  
 Constants Used in the Evaluation of the Free Volume Fractions of Polymer and Solvent

Polymer	Solvent	Concentration range ( $w_2$ )	Temperature range, °C.	Molecular weight range $\times 10^{-3}$	$T_g$ , °K.		$10^4 \times \alpha_f$ , deg. <sup>-1</sup>	
					Polymer	Solvent	Polymer	Solvent
Polyisobutylene <sup>a</sup>	Isooctane	0.05-1.0	20	0.9-1200	200 <sup>b</sup>	104 <sup>c</sup>	5.0	9 <sup>d</sup>
Poly(decamethylene adipate) <sup>e</sup>	Diethyl succinate	0-1.0	79	16	175 <sup>c</sup>	173 <sup>o</sup>	7.2	10 <sup>d</sup>
Poly(ethyl methacrylate) <sup>f</sup>	Diethyl phthalate	0.1-1.0	1-150	--	338 <sup>g</sup>	188 <sup>h</sup>	3.0	8.2
Poly(butyl methacrylate) <sup>f</sup>	Diethyl phthalate	0-1.0	10-120	111	293 <sup>g</sup>	188 <sup>h</sup>	4.8	8.2
Poly(vinyl acetate) <sup>f,j</sup>	Diethyl phthalate	0.1-1.0	50-157 <sup>i</sup>	8-1300 <sup>i</sup>	305 <sup>k</sup>	188 <sup>h</sup>	5.0	8.2
			10-100 <sup>j</sup>	99 <sup>j</sup>				
Poly(methyl acrylate) <sup>l</sup>	Diethyl phthalate	0-1.0	20-100	130	282	188 <sup>h</sup>	4.8	8.2

<sup>a</sup> Data of Tager et al.<sup>25</sup>

<sup>b</sup> For the lowest molecular weight sample  $T_g$  was estimated to be 150°K.

<sup>c</sup> Estimated from  $T_g$  of similar compounds<sup>24</sup> or from  $T_g = 0.65T_m$ .<sup>22</sup>

<sup>d</sup> Estimated from  $\alpha_f - \alpha_g$  of similar solvents.

<sup>e</sup> Data of Flory.<sup>26</sup>

<sup>f</sup> Data of Fujita.<sup>28</sup>

<sup>g</sup> See Rogers and Mandelkern.<sup>29</sup>

<sup>h</sup> See Garfield and Petrie.<sup>12</sup>

<sup>i</sup> Data of Fox and Allen.<sup>30</sup>

<sup>j</sup> Data of Kishimoto.<sup>31</sup>

<sup>k</sup> Value of  $f_g = 0.028$ .<sup>18</sup>

<sup>l</sup> Data of Fujita and Maekawa.<sup>32</sup>

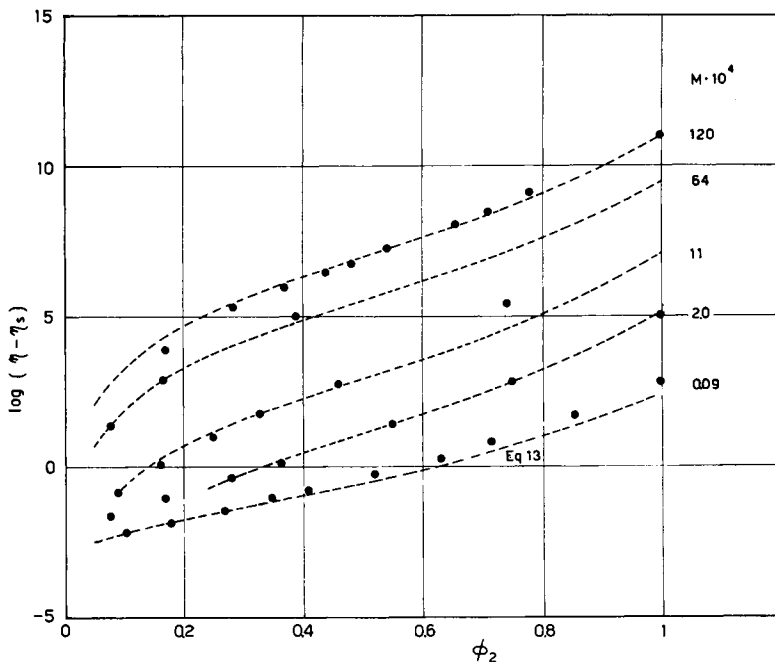


Fig. 5. Logarithm of  $(\eta - \eta_s)$  plotted against the polymer volume fraction  $\phi_2$  for the polyisobutylene-isooctane solutions.<sup>25</sup> Figures denote molecular weight of the polymers: (●) experimental points; (- -) eqs. (12) and (13) at 20°C.

The first equation applies from  $w_2 = 0.3$  to  $w_2 = 1$ , the second in a relatively narrow range of low concentrations. A gradual transition from one theoretical curve to the other characterizes the viscosity data.

### Poly(ethyl Methacrylate)-Diethyl Phthalate

Some data on the system poly(ethyl methacrylate)-diethyl phthalate (DEP), supplied in numerical form by Fujita,<sup>28</sup> are plotted in Figure 8 together with the curve described by eq. 12. In the range of temperatures going from 1 to 150°C., the theoretical equation applies quite successfully from  $w_2 = 0.2$  up to  $w_2$  of the order of 0.9. The values of  $\log B$  show a slight dependence on temperature.

Two sets of data, obtained well below the glass transition temperature of the polymer (65°C.) can be used to show that under these conditions the free volume fraction of the polymer  $f_2$  must be calculated by eq. (3) in order to attain the correct theoretical description. In Figure 9 the viscosities measured at 1 and at 20°C. are compared with the corresponding curves of Figure 8 [calculated with  $f_2$  values given by eq. (3)] and also with two theoretical curves calculated by assuming for  $f_2$  the "universal" value of  $f_\theta = 0.025$  (which has been suggested to remain constant below  $T_\theta$ <sup>18</sup>). It is apparent that the second procedure must be discarded.

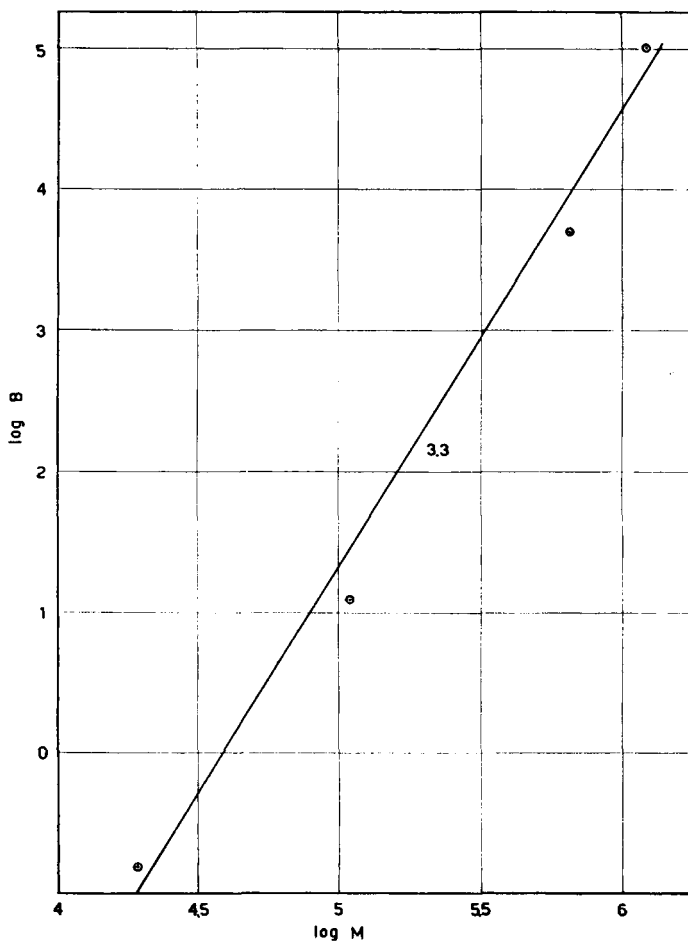


Fig. 6. Log  $B$ , as derived from Figure 5 plotted against log  $M$  of the polyisobutylene samples.

### Poly(butyl Methacrylate)-DEP

Data on the poly(butyl methacrylate)-DEP system, extending over the entire concentration range,<sup>28</sup> may illustrate the validity of both eqs. (12) and (13). The first equation is compared in Figure 10 with the experimental points, while eq. (13) is plotted, together with the viscosity data, in Figure 11. From  $w_2 = 0.3$  and up to undiluted polymer, the agreement between eq. (12) and experiment is good, and in the range of weight fractions from 0.01 to 0.1 there is a satisfactory agreement with eq. (13). The values of log  $B$  and log  $B'$  varies slowly with temperature. As found previously for other systems, there is no evidence in the experimental data of a sudden transition from the flow region described by eq. (13) to that described by eq. (12).

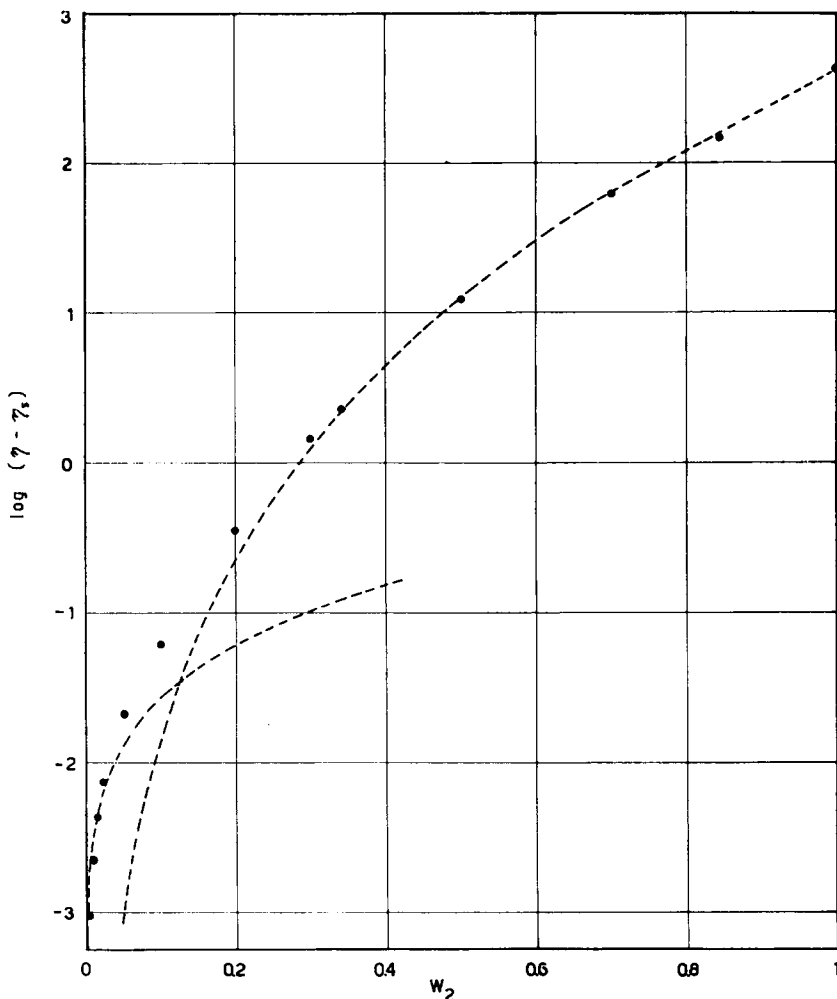


Fig. 7. Logarithm of  $(\eta - \eta_0)$  plotted against  $w_2$  for the poly(decamethylene adipate)-diethyl succinate system;<sup>26</sup> (---) eqs. (12) and (13) at 79°C.; (●) experimental data.

**Poly(vinyl Acetate)-DEP**

Fox and Allen<sup>30</sup> have reported in algebraic form their results on this system. Samples varying in molecular weight from 8000 to  $1.3 \times 10^6$  were studied in the range of temperatures from 50 to 157°C. The multi-constant empirical equation used by Fox and Allen is compared in Figure 12 with eq. (12) for a sample having a molecular weight of  $10^5$  at three temperatures. An excellent fit is found over a large range of concentration in any case. A similar comparison for a sample having molecular weight of 8000 is also shown in Figure 12 for eq. (13) which fits well the experimental data up to a volume fraction of 0.6. The same theoretical curves fit the data reported by Kishimoto<sup>31</sup> for the poly(vinyl acetate)-DEP system

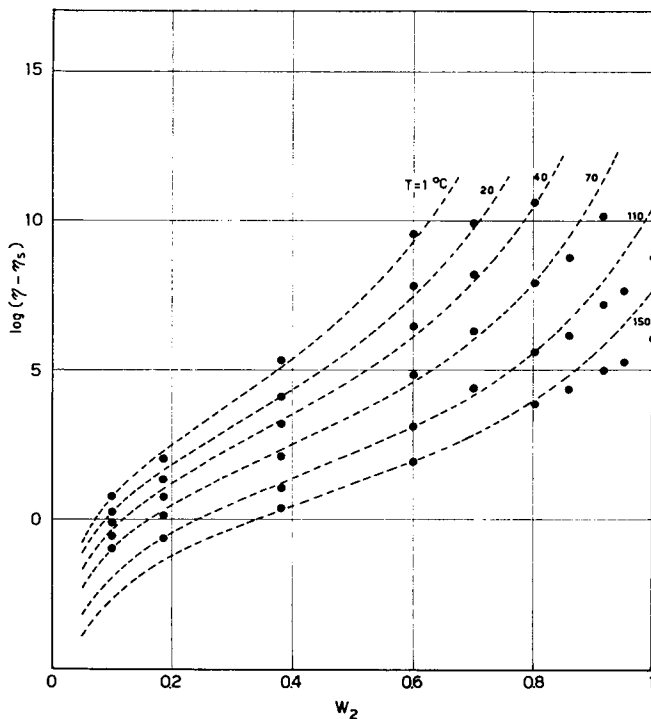


Fig. 8. Logarithm of  $(\eta - \eta_s)$  plotted against  $w_2$  for the poly(ethylmethyl acrylate)-DEP system:<sup>28</sup> (--) eq. (12) at the temperatures indicated; (●) experimental data.

over large ranges of concentration and at temperatures varying from 10 to 100°C. (see Fig. 13).

### Poly(methyl Acrylate)-DEP

The results obtained for this system by Fujita and Maekawa<sup>32</sup> are shown in Figure 14. For all the temperatures explored the agreement is satisfactory from weight fraction 0.3 up to undiluted polymer. Deviations from the experimental data are found only at 20°C. for the high concentration range, where the viscosities are of the order of  $10^{10}$  poises and the experimental accuracy can be low. A satisfactory comparison with eq. (13), not shown in Figure 14, is also found at low concentrations. Other polymer-solvent systems for which data are available only over limited concentration ranges have been also reviewed, and the results were found to be similar to those discussed above.

### CONSIDERATIONS OF THE FREE-VOLUME TREATMENT

The examples shown above demonstrate that the free-volume treatment can predict with considerable accuracy the viscometric properties of many different systems. It must be noted that in some cases the experimental

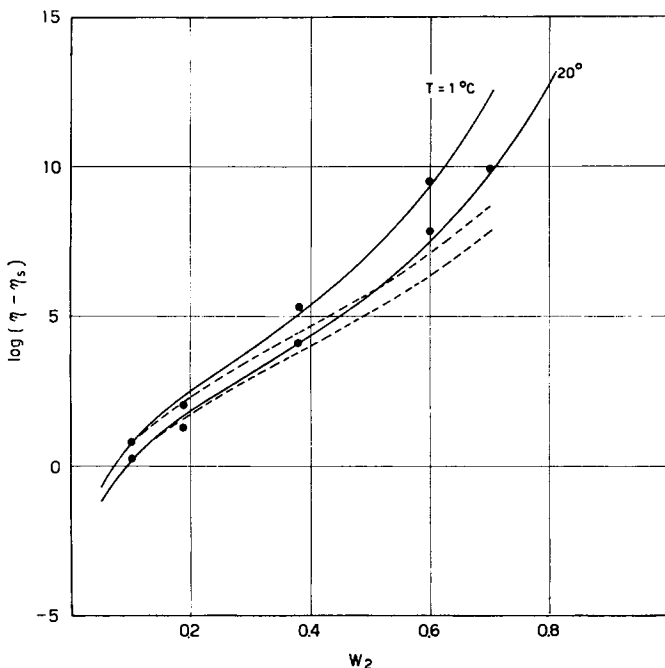


Fig. 9. Logarithm of  $(\eta - \eta_s)$  at temperatures below the  $T_g$  of the polymer, plotted against  $w_2$  for the system of Fig. 8. (—) eq. (12) with values of  $f_2$  derived by means of eq. (3); (---) eq. (12) with  $f_2 = 0.025$ ; (●) experimental data.

data have been successfully described over very large ranges of molecular weight (from  $10^8$  to  $10^6$ ), of concentration, of temperature (from 0 to  $150^\circ\text{C}$ .), and sometimes over the viscosity range of  $10^{10}$ -fold, as in Figure 10.

While the agreement between theory and experiment supports the substantial validity of the treatment, it may be interesting to review the assumptions on which eqs. (12) and (13) are based: (a) the flow of polymer solutions below and above the critical concentration of chain entanglements is described by the Bueche equations, eqs. (7) and (10); (b) the temperature and concentration dependence of the friction coefficient of a polymeric chain in solution is determined by the free volume of the solution through the Doolittle equation eq. (2); (c) the fractional free volume of the solution is the sum of the free volume fractions of the components in their unmixed states [eq. (11)]; (d) the glass transition temperature  $T_g$  represents for both polymer and solvent an "iso-free volume" state. Above  $T_g$  the fractional free volume is a linear function of temperature in the form given by eq. (3), which applies, as shown previously, also between  $T_g$  and  $T_g$ .

Assumptions (a) and (b) are justified if it is kept in mind that the first one is supported by the successes obtained by the application of the Bueche concept of coupling entanglements to the interpretation of the molecular

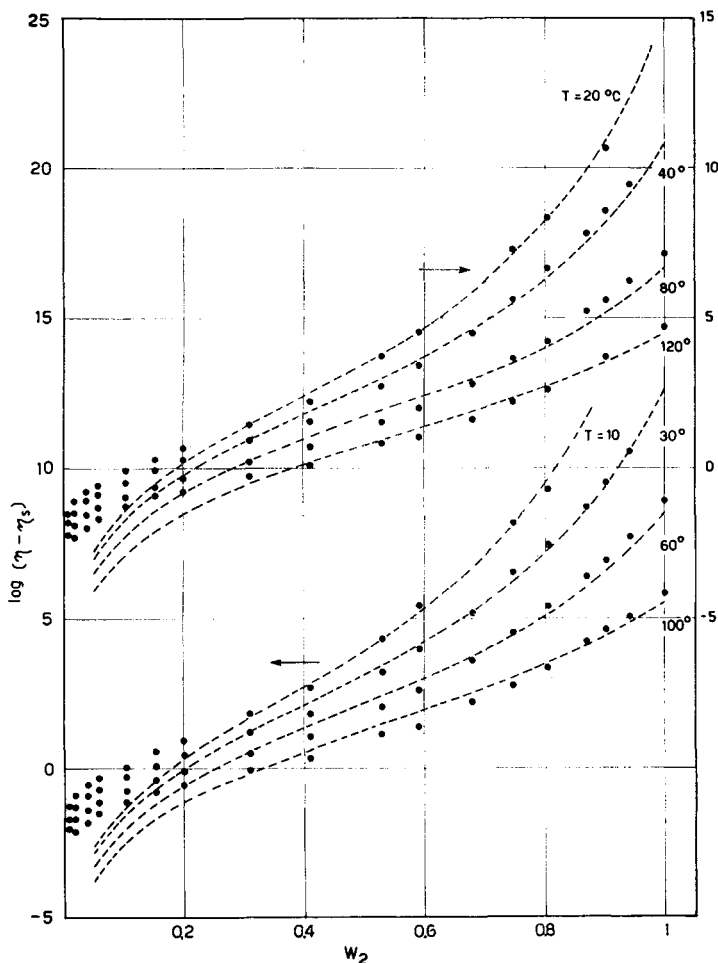


Fig. 10. Logarithm of  $(\eta - \eta_0)$  plotted against  $w_2$  for the poly(butyl methacrylate)-DEP system:<sup>28</sup> (---) eq. (12); (●) experimental data.

weight dependence of the viscosity of polymer melts,<sup>15,33</sup> and the second one by its widespread application not only to the viscosity of simple liquids and of polymer melts,<sup>11</sup> but to the diffusion of gases in polymers,<sup>34</sup> the retarded volume contraction of a polymer cooled rapidly to temperatures near  $T_g$ ,<sup>35</sup> the dielectric relaxation processes in polymers and plasticized polymers,<sup>14</sup> and the electrical conductance in fused salts.<sup>36</sup>

Assumption (c), concerning the additivity of free volumes, can be considered to be only a first approximation. It was shown previously<sup>1</sup> that the total volumes are additive within 0.2% for the system PVC-cyclohexanone, but there may be relatively large volume contractions for plasticized PVC<sup>14</sup> or for other polymer solutions.<sup>37</sup> However, for the systems examined in this work the assumption of additivity seems to be relatively justified by the results obtained.



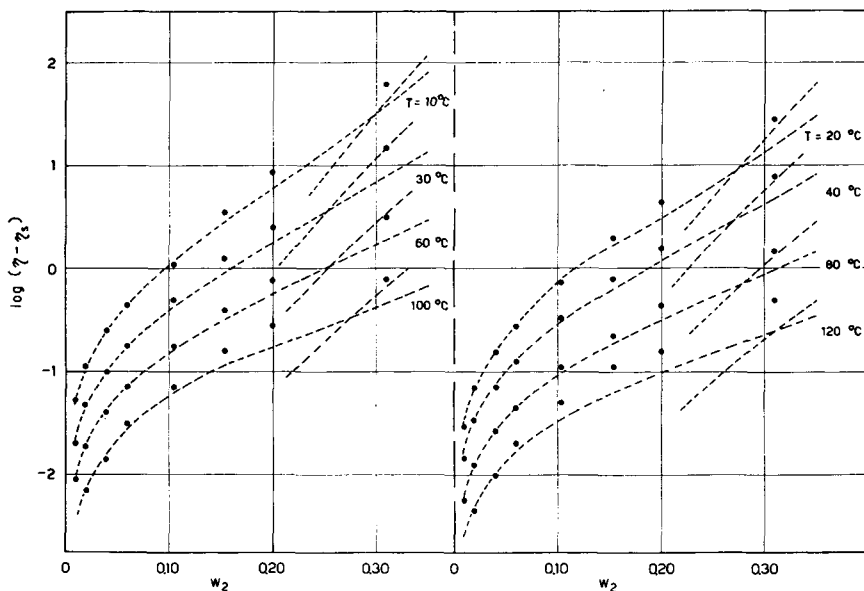


Fig. 11. Logarithm of  $(\eta - \eta_s)$  plotted against  $w_2$  for the system of Fig. 10: (---) eq. 13 (at low concentrations) and eq. (12) (at  $w_2 > 0.25$ ); (●) experimental data.

Assumption (d) is widely accepted,<sup>10,11,13,18</sup> but the "constant" fractional free volume at  $T_g$  has been defined in different ways, and three substantially different values of  $f_g$  have been reported: 0.025,<sup>11,13,14,38</sup> 0.12,<sup>34,39-41</sup> and 0.20.<sup>42</sup> These discrepancies result from the different models and assumptions used in evaluating  $f_g$ . It must be pointed out that only the first value can be applied successfully in the present interpretation of the viscosity of polymer solutions. The value of  $T_g$  for low molecular weight solvents varies from approximately 80°K. for hydrocarbons to 110°K. for alcohols, 150°K. for glycols, and 190-250°K. for typical plasticizers of the phthalic ester series.<sup>12,24,41</sup> The value of  $\alpha_l$  for many liquids is approximately  $1.3 \times 10^{-3} \text{ deg.}^{-1}$ ,<sup>6,13,43</sup> The expansion coefficient of the crystalline solids, practically equal to that of the glasses, is  $2-4 \times 10^{-4} \text{ deg.}^{-1}$ ,<sup>44</sup> so that for solvents the expansion coefficient of free volume should be approximately  $10^{-3} \text{ deg.}^{-1}$ , as assumed by Kelley and Bueche. An independent confirmation of the correctness of this value can be derived from the data on free volume of benzene and  $\text{CCl}_4$  reported by Miller<sup>45</sup> for different temperatures and calculated from the data of Bridgman on the pressure dependence of viscosity. In conclusion, the assumptions listed above can be considered reasonable for systems for which there are no strong interactions between polymer and solvents leading to large volume changes in the solution process.

## DISCUSSION

In some previous analyses of the viscometric properties of concentrated polymeric solutions empirical reduction schemes have been used to relate

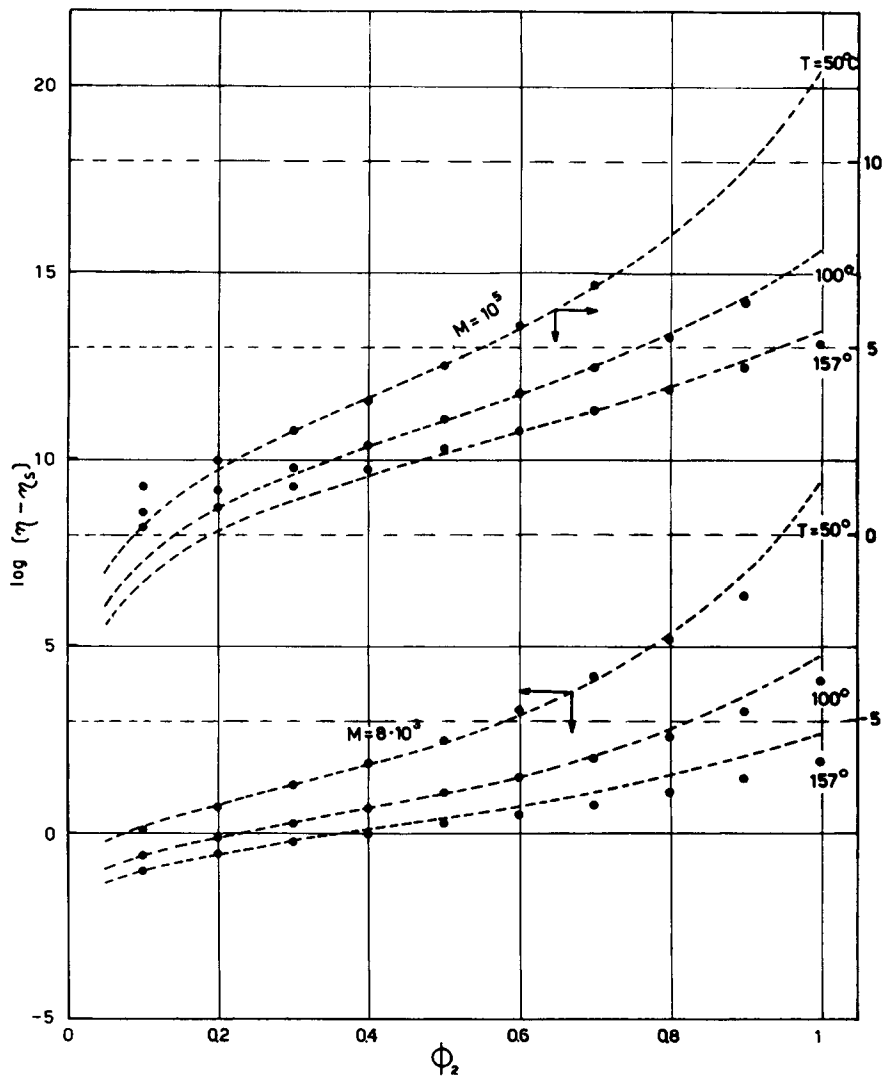


Fig. 12. Logarithm of  $(\eta - \eta_s)$  plotted against  $\phi_2$  for the poly(vinyl acetate)-DEP system:<sup>30</sup> (●) experimental data derived from the empirical equation given by Fox and Allen:<sup>30</sup> (---) eq. (12) for the upper part of the figure ( $M = 10^5$ ) and eq. (13) for the lower part ( $M = 8000$ ).

the solution viscosity to the polymer concentration and molecular weight.<sup>1,18</sup> The results obtained in the present work show conclusively that a treatment based on free-volume concepts can interpret with considerable accuracy the experimental data for widely different polymer solutions, and therefore it eliminates the need for empirical correlations. The Kelley-Bueche equation, eq. (12), which should hold for solutions in which the macromolecules are entangled, can usually be applied above

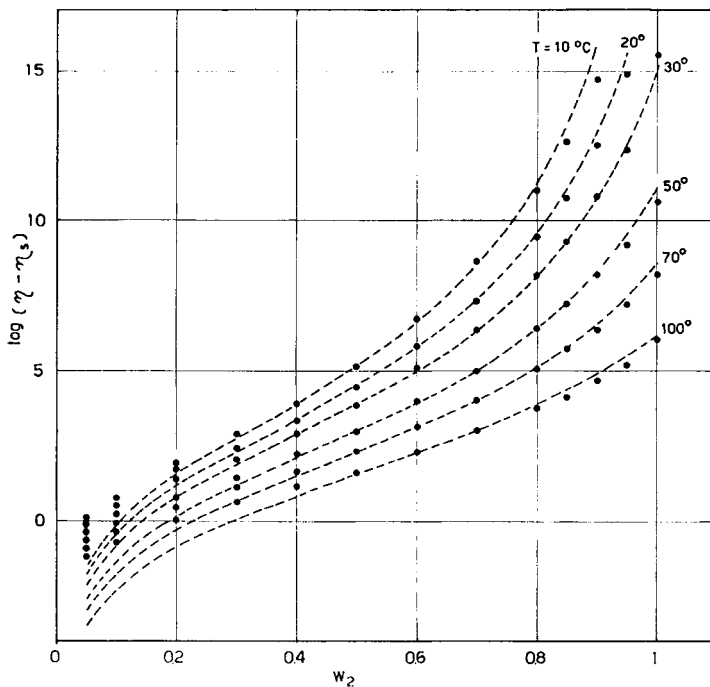


Fig. 13. Logarithm of  $(\eta - \eta_s)$  plotted against  $w_2$  for the poly(vinyl acetate)-DEP system:<sup>31</sup> (---) eq. (12); (●) experimental data.

approximately the polymer weight fraction 0.3, but for some systems it can be applied down to  $w_2$  as low as 0.05 (see Fig. 1) or 0.1 (Figs. 5 and 8). It may be observed that the lower limit of validity of eq. (12) corresponds to solution viscosities of the order of 1–10 poises. At lower concentrations the molecular chains should not be entangled, and eq. (13) should apply. However the sharp transition from one flow region to the other required by the theory is not observed experimentally, and eq. (13) holds only below a portion of the experimental curves which remains unpredicted by the theory.

For polymer melts, an abrupt change in the molecular weight dependence of viscosity is normally found at the critical chain length above which a network structure is formed through intermolecular entanglements.<sup>15</sup> However, for dimethylpolysiloxanes<sup>46</sup> and poly(vinyl acetate),<sup>47</sup> the transition is rather gradual, as found in the present work for the concentration dependence of viscosity (Figs. 1–3, 7,11). This could be interpreted as evidence that for some systems the entanglement network can be formed only gradually with increasing chain length or concentration of the polymer.

The flow region over which eq. (13) is applicable is limited to  $w_2$  lower than 0.05. It extends to polymer weight fractions of 0.1 for the DEP solutions of poly(butyl methacrylate)(molecular weight 110,000, and to

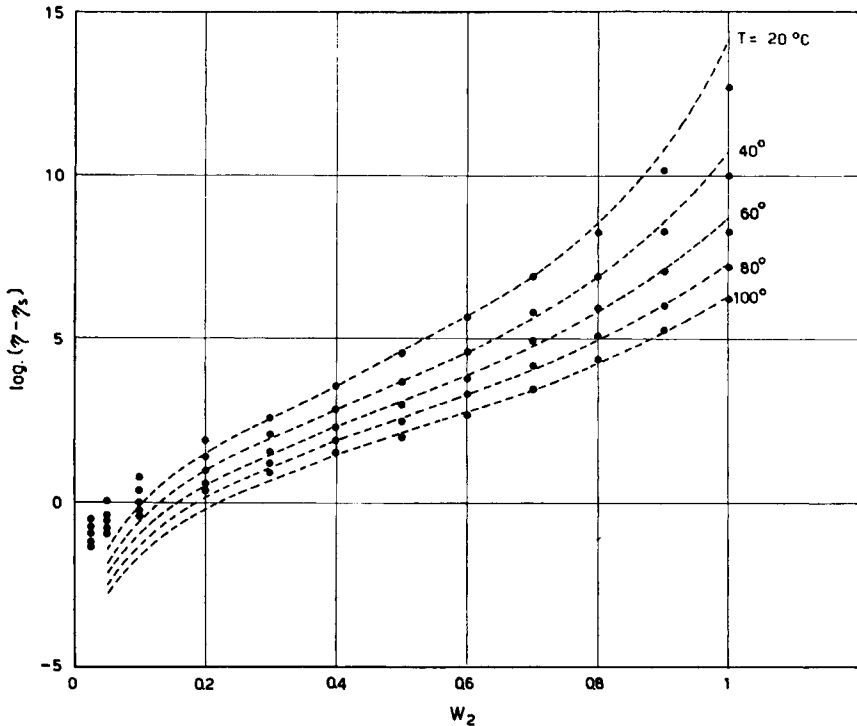


Fig. 14. Logarithm of  $(\eta - \eta_s)$  plotted against  $w_2$  for the poly(methyl acrylate)-DEP system:<sup>32</sup> (--) eq. (12); (●) experimental data.

0.15 for the cyclohexanone solutions of the PVC sample having the lowest molecular weight,  $M_w = 10,500$ . For the poly(vinyl acetate)-DEP solutions investigated by Fox and Allen, the applicability of eq. (13) to a sample having  $M = 8000$  goes up to polymer volume fractions of 0.6–0.8, as may be seen in Figure 12. For these solutions, apparently, the macromolecules do not entangle until such high concentrations are reached.

For a given polymer-solvent system the critical concentration for chain entanglements should be approximately inversely proportional to the polymer molecular weight.<sup>18</sup> This can be demonstrated, for the PVC-cyclohexanone solutions, by plotting on a log-log paper the critical volume fraction  $\phi_2^*$  at which the curves of eqs. (12) and (13) cross each other, against the polymer molecular weight  $M_w$ . As shown in Figure 15, one obtains a straight line which is described by the equation:

$$\phi_2 M_w = 4000 \quad (14)$$

from which the critical molecular weight for chain entanglement in the undiluted polymer results to be approximately 4000.

From Figure 7 it is seen that the corresponding figure for the poly(decamethylene adipate) is approximately 2000, while a much larger molecular weight between entanglements is derived from Figure 11 for poly(butyl

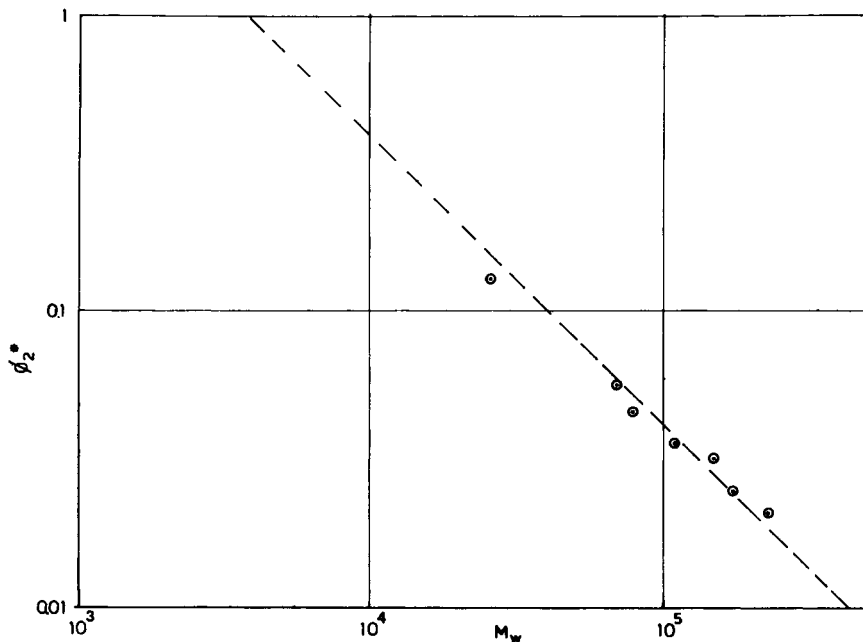


Fig. 15. Logarithm of the critical fraction  $\phi_2^*$  (see text) plotted against the logarithm of the molecular weight  $M_w$  of the PVC samples of Table I.

methacrylate) i.e., 30,000. From Figure 11 it may be seen also that the critical concentration for chain entanglement is substantially temperature-independent in the range of temperature of 10–120°C. for this system.

In all the examples shown in the present paper, the theoretical curves were adjusted to fit the experimental results over a given range of concentration. This required only changing the value of the parameters  $B$  and  $B'$ , while the form of the curve, being not adjustable, provided the critical test of the agreement between theory and experimental data. The empirical parameters  $B$  and  $B'$ , as shown in Figures 4 and 6, depend on the 3.5 and 1.0 power of molecular weight. It may be seen from Table III that they vary only slightly with temperature [the maximum activation energy is found to be of the order of 3000 cal./mole, for the poly(butyl methacrylate)–DEP solutions of Figure 10] and as a first approximation, therefore, the values of  $B$  and  $B'$  for a given system can be considered independent of temperature.

In order to compare their values for different polymer–solvent systems, they can be written:

$$B = K_2 Z^{3.5} \quad (15)$$

$$B' = K_2' Z \quad (16)$$

where  $Z$  is the number of atoms in the chain (for vinyl polymers  $Z$  is twice the number of monomer units in the chain), and for polydisperse polymers

TABLE III  
Values of the Parameters  $B$ ,  $B'$ , and  $K_z$ ,  $K_z'$  (see text) for  
Several Polymer-Solvent Systems

Polymer	Solvent	$M \times 10^{-3}$	$T$ , °C.	$\log B$	$\log B'$	$\log K_z$	$\log K_z'$
Polyisobutylene	Isooctane	1200	20	5.1	—	-11.1	—
		640	20	3.7	—	-11.6	—
		110	20	1.1	—	-11.5	—
		20	20	-0.8	-2.85	-10.8	-5.7
		0.9	20	—	-3.50	—	-5.0
Poly(decamethylene adipate)	Diethyl succinate	16	79	-0.05	-2.70	-10.6	-5.7
		—	—	—	—	—	—
Poly(ethyl methacrylate)	Diethyl phthalate	—	1	-0.60	—	—	—
		—	20	-0.35	—	—	—
		—	40	-0.25	—	—	—
		—	70	-0.25	—	—	—
		—	110	-0.55	—	—	—
Poly(butyl methacrylate)	Diethyl phthalate	111	10	-2.15	-3.57	-13.3	-6.7
		—	20	-1.9	-3.47	-13.1	-6.7
		—	30	-1.7	-3.37	-12.9	-6.6
		—	40	-1.65	-3.25	-12.8	-6.4
		—	60	-1.4	-3.10	-12.6	-6.3
		—	80	-1.5	-3.10	-12.7	-6.3
		—	100	-1.3	-2.92	-12.5	-6.1
Poly(vinyl acetate) <sup>a</sup>	Diethyl phthalate	1300	50	4.30	—	-11.4	—
		1300	100	4.25	—	-11.4	—
		1300	157	4.40	—	-11.3	—
		100	50	0.50	—	-11.3	—
		100	100	0.40	—	-11.4	—
		100	157	0.50	—	-11.3	—
		8	50	—	-2.30	—	-4.6
		8	100	—	-2.30	—	-4.6
		8	157	—	-2.10	—	-4.4
		Poly(vinyl acetate) <sup>b</sup>	Diethyl phthalate	99	10	-0.8	-2.97
—	20			-0.8	—	-12.6	—
—	30			-0.8	—	-12.6	—
—	40			-0.9	—	-12.7	—
—	50			-0.9	—	-12.7	—
—	60			-0.95	—	-12.7	—
—	70			-0.9	—	-12.7	—
—	80			-1.0	—	-12.8	—
—	90			-1.0	—	-12.8	—
—	100			-1.0	-2.50	-12.8	-5.9
Poly(methyl acrylate)	Diethyl phthalate	130	20	-0.5	-2.92	-12.7	-6.4
		—	40	-0.4	-2.62	-12.6	-6.1
		—	60	-0.3	-2.42	-12.5	-5.9
		—	80	-0.3	-2.37	-12.5	-5.8
		—	100	-0.3	-2.27	-12.5	-5.8

<sup>a</sup> Data of Fox and Allen.<sup>30</sup>

<sup>b</sup> Data of Kishimito.<sup>31</sup>

the correct average  $Z$  is, of course, the weight average.<sup>15</sup> The values of  $\log K_z$  and  $\log K_z'$  are shown in Tables I and III, and it may be seen that they are relatively constant for all the systems examined. Averaging the values within any polymer-solvent system and averaging again the figures obtained in this way, gives for the average "universal" values of  $K_z$  and  $K_z'$ :

$$\log K_z = -11.8 \pm 0.7 \quad (17)$$

$$\log K_z' = -5.75 \pm 0.5 \quad (18)$$

where the deviations are average deviations calculated from all the data of Tables I and III. It may be observed that with the values given by the relations (17) and (18) it is possible to calculate, on completely theoretical grounds, the viscosity of any polymeric system, within a factor of approximately 5, at any molecular weight and temperature, and at any concentration, except for the region around  $C^*$  where the theoretical curves cross each other. Taking into account the magnitude of the possible errors introduced in the evaluation of  $\log K_z$  and  $\log K_z'$  by the approximate characteristics of the free-volume treatment, by the effects due to the polydispersity of the polymers investigated (use of approximated  $M_w$ ), and by the visual fitting of the theoretical curves to the experimental data, the relative constancy of the values of these parameters can be considered remarkable (see Tables I and III). While this constancy should be related to the constancy of the free volume and of the segmental mobility of the macromolecules in given standard states, the understanding of its exact physical meaning is not easy and requires further investigations.

As may be derived from the data of Table II, eqs. (12) and (13) can be successfully applied to polymeric solutions for which the free volume fraction of the polymer  $f_2$  has values lying between zero [for poly(vinyl chloride) at 30°C. and for poly(ethyl methacrylate) at 1°C.] and approximately 0.09 [for polyisobutylene at 20°C. and for poly(vinyl acetate) at 157°C.], with the single high figure of 0.16 for poly(decamethylene adipate) at 79°C. The free volume fractions of the solvent  $f_1$  are in the range 0.10–0.22, so that the total fractional free volume of the solutions can be seen to vary within the range 0.03–0.21.

The free-volume treatment of polymer solutions can be therefore applied even when the total free volume fraction  $F = \phi_2 f_2 + \phi_1 f_1$  is as high as 0.2, while it has been predicted,<sup>48</sup> by analogy with the well-known limitation of the applicability of the WLF equation (5) to values of  $f_2$  lower than 0.08, that the application of free volume concepts to polymeric solutions would be limited to values of  $F$  lower than 0.08.

In the Kelley-Bueche treatment, the effects of temperature, concentration, molecular weight, and solvent type on viscosity are assumed to be due to changes of free volume and of entanglement couplings between the macromolecules. Fujita and Kishimoto<sup>49</sup> have also interpreted, on the basis of free volume, the concentration dependence of the viscosity and of

the diffusion coefficients of concentrated polymeric solutions. Their equation can be written

$$\frac{1}{\ln(\eta_0\phi_2/\eta)} = f_2 + \frac{(f_2)^2}{(f_1 - f_2)(1 - \phi_2)} \quad (19)$$

where  $\eta_0$  is the viscosity of the polymer and  $\eta$  the viscosity of the solution at the volume fraction  $\phi_2$ . In the Fujita-Kishimoto equation the free volume fractions of polymer and solvent  $f_2$  and  $f_1$  are treated as experimental parameters, which can be determined from the linear plot of the left side of eq. (19) against  $(1 - \phi_2)^{-1}$ . Equation (19) can be derived directly from the Kelley-Bueche equation, eq. (13), and it should therefore be applicable only to nonentangled solutions. The equivalent equation for entangled solutions, derived from eq. (12), is

$$\frac{1}{\ln(\eta_0\phi_2^4/\eta)} = f_2 + \frac{(f_2)^2}{(f_1 - f_2)(1 - \phi_2)} \quad (20)$$

which differs from eq. (19) by the additive term  $\ln \phi_2^3$  on the denominator of the left side. The difference can be, in some cases, relatively small for high concentrations of polymer in the solutions, and it has been shown in effect by Fujita and Maekawa<sup>32</sup> that their data on the poly(methyl acrylate)-DEP system can be correctly described by eq. (19) only over relatively narrow ranges of concentration ( $\phi_2$  larger than 0.7-0.8). For comparison, it must be noted that eq. (12) describes the same data over a range of concentration much broader ( $w_2$  greater than 0.3), as may be seen in Figure 14.

## CONCLUSION

The results described in the present work show the usefulness of the free-volume concept in the study of polymeric systems. The Kelley-Bueche equations, eqs. (12) and (13), represent an important extension of the Bueche equation, eq. (6) (which describes the molecular weight dependence of viscosity for molten polymers) and of the Williams-Landel-Ferry equation, eq. (5) (which gives the temperature dependence of the viscosity of molten polymers). It may be seen in fact that both equations are the limiting form of the eqs. (12) and (13) for  $\phi_2 = 1$ .

The treatment discussed above is limited, of course, to solutions in which the volume additivity is a reasonable assumption or has been experimentally verified, but it applies well to solutions where the fractional free volume  $F'$  is as high as 0.2. It gives, therefore, an adequate representation of polymer solutions within very large ranges of concentration and temperatures.

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## References

1. Pezzin, G., and N. Gligo, *J. Appl. Polymer Sci.*, **10**, 1 (1966).
2. Kelley, F. N., and F. Bueche, *J. Polymer Sci.*, **50**, 549 (1961).
3. Brush, S. F., *Chem. Rev.*, **62**, 513 (1962).
4. Frenkel, J., *Kinetic Theory of Liquids*, Dover, New York, 1955.
5. Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1954.
6. Weyman, H. D., *Kolloid-Z.*, **181**, 131 (1962).
7. Batschinski, A. J., *Z. Physik. Chem.*, **84**, 643 (1913).
8. Doolittle, A. K., *J. Appl. Phys.*, **22**, 1471 (1951).
9. Bueche, F., *J. Chem. Phys.*, **24**, 418 (1956).
10. Cohen, M. H., and D. Turnbull, *J. Chem. Phys.*, **31**, 1164 (1959).
11. Williams, M. L., R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).
12. Garfield, L. J., and S. E. Petrie, *J. Phys. Chem.*, **68**, 1750 (1954).
13. Kovacs, A. J., *Fortschr. Hochpolymer. Forsch.*, **3**, 394 (1963).
14. Saito, S., Res. Electrotechn. Labor. No. 648, Tokyo, 1964.
15. Fox, T. G., S. Gratch, and S. Loshaek, in *Rheology* Vol. I, F. R. Eirich, Ed., Academic Press, New York, 1956.
16. Bueche, F., *Physical Properties of Polymers*, Interscience, New York, 1962.
17. Rouse, P. E., Jr., *J. Chem. Phys.*, **21**, 1272 (1953).
18. Ferry, J. D., *Viscoelastic Properties of Polymers*, Wiley, New York, 1961.
19. Wood, L. A., *J. Polymer Sci.*, **28**, 319 (1958).
20. Garbuglio, C., A. Rodella, G. C. Borsini, and E. Gallinella, *Chim. Ind. (Milan)*, **46**, 166 (1964).
21. Bueche, F., *J. Chem. Phys.*, **20**, 1959 (1952).
22. Jenckel, E., *Kolloid-Z.*, **130**, 64 (1953).
23. Illers, K. H., *Rheol. Acta*, **3**, 185 (1964).
24. Wunderlich, B., *J. Phys. Chem.*, **64**, 1052 (1960).
25. Tager, A. A., V. E. Dreval, N. G. Trayanova, *Dokl. Akad. Nauk SSSR*, **151**, 140 (1963).
26. Flory, P. J., *J. Phys. Chem.*, **46**, 870 (1942).
27. Garfield, L. J., S. E. Petrie, and D. W. Vanas, *Trans. Soc. Rheol.*, **6**, 131 (1962).
28. Fujita, H., private communication.
29. Rogers, S. S., and L. Mandelkern, *J. Phys. Chem.*, **61**, 985 (1957).
30. Fox, T. G., and V. R. Allen, paper presented at 140th Meeting, American Chemical Society, Chicago, Sept. 1961.
31. Kishimoto, A., *J. Polymer Sci.*, **A2**, 1421 (1964).
32. Fujita, H., and E. Maekawa, *J. Phys. Chem.*, **66**, 1053 (1962).
33. Bueche, F., and F. N. Kelley, *J. Polymer Sci.*, **45**, 267 (1960).
34. Kumins, C. A., and J. Roteman, *J. Polymer Sci.*, **55**, 699 (1961).
35. Kovacs, A. J., *Compt. Rend.*, **250**, 109 (1960); *Trans. Soc. Rheol.*, **5**, 285 (1961).
36. Angell, C. A., *J. Phys. Chem.*, **68**, 1917 (1964).
37. Baker, C. H., W. B. Brown, G. Gee, J. S. Rowlinson, D. Stubley, and R. E. Yeadon, *Polymer*, **3**, 215 (1962).
38. Miller, A. A., *J. Polymer Sci.*, **A2**, 3159 (1964).
39. Simha, R., and R. F. Boyer, *J. Chem. Phys.*, **37**, 1003 (1962).
40. Wunderlich, B., D. M. Bodily, and M. H. Kaplan, *J. Appl. Phys.*, **35**, 95 (1964).
41. Bondi, A., *J. Polymer Sci.*, **A2**, 3159 (1964).
42. Kanig, G., *Kolloid-Z.*, **190**, 1 (1963).
43. *Handbook of Chemistry and Physics*, Chemical Rubber Publishing Co., Cleveland, 1960.
44. *International Tables for X-Ray Crystallography*, Vol. III, Kynoch Press, Birmingham, 1962.

45. Miller, A. A., *J. Phys. Chem.*, **67**, 2809 (1963).
46. Werker, R. L., *J. Polymer Sci.*, **22**, 353 (1956).
47. Ninomiya, K., J. D. Ferry, and Y. Oyanagi, *J. Phys. Chem.*, **67**, 2297 (1963).
48. Ferry, J. D., and R. A. Stratton, *Kolloid-Z.*, **171**, 107 (1960).
49. Fujita, H., and A. Kishimoto, *J. Chem. Phys.*, **34**, 393 (1961); H. Fujita, *Fortschr. Hochpolymer. Forsch.*, **3**, 1 (1961).

### Résumé

Les données obtenues au cours d'une étude précédente sur les propriétés viscosimétriques de solutions concentrées de chlorure de polyvinyle dans la cyclohexanone ont été interprétées sur la base du traitement du volume libre de Kelley-Bueche. On a montré que la dépendance de la viscosité en fonction de la concentration et du poids moléculaire dans ce système peut être prédite avec une précision remarquable. Une extension de ce traitement permet la description de solutions relativement diluées. Les équations du volume libre ont été appliquées à un nombre de données concernant des solutions polymériques, disponibles dans la littérature, et ont été trouvées applicables dans de larges domaines de viscosité/température et de poids moléculaires.

### Zusammenfassung

Die in einer vorhergehenden Untersuchung erhaltenen Daten für die viskosimetrischen Eigenschaften konzentrierter Polyvinylchloridlösungen in Zyklohexanon wurden auf der Grundlage der auf dem freien Volumen beruhenden Behandlung nach Kelley und Bueche interpretiert. Es wurde gezeigt, dass die Konzentrations- und Molekulargewichtsabhängigkeit dieses Systems mit bemerkenswerter Genauigkeit vorausgesagt werden kann. Die Erweiterung der Behandlung erlaubt die Beschreibung relativ verdünnter Lösungen. Die auf dem freien Volumen beruhenden Gleichungen wurden auf eine Anzahl von in der Literatur vorhandenen Daten über Polymerlösungen in einem sehr grossen Viskositäts-, Temperatur-, und Molekulargewichtsbereich mit Erfolg angewendet.

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