

FREE VOLUME METHODS IN THE ANALYSIS  
OF THE VISCOSITY-CONCENTRATION DEPENDENCE  
OF POLY(DIMETHYLSILOXANE) SOLUTIONS\*

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Two methods for the determination of the free volume parameters of pure components were evaluated from measurements of the viscosities of poly(dimethylsiloxane) solutions over a wide concentration range from dilute solutions to pure polymer. The method using pure polymer as the reference concentration yielded a result comparable to the value obtained from measurements of the temperature dependence of the viscosity of the melt. On the other hand, an infinitely dilute solution was found to be quite inadequate as reference concentration.

In terms of the free volume theory the viscosity of a polymer melt can be expressed by Doolittle's relationship<sup>1</sup>

$$\ln \eta = \ln A + B/f, \quad (1)$$

where  $f$  is the fractional free volume defined as the ratio of the free volume to the overall volume of the polymer melt,  $A$  and  $B$  are constants independent of temperature. The constant  $A$  includes the structure factor and the characteristic frictional coefficient of Allen and Fox's equation<sup>2</sup>, the term  $B/f$  is analogous to the term  $1/\alpha(T - T_0)$  in Vogel's empirical relationship<sup>3,4</sup> describing the temperature dependence of viscosity. The parameters  $\alpha$  and  $T_0$  depend on the molecular weight and concentration of the polymer.

The applicability of Doolittle's relationship or Allen and Fox's equation is not restricted to polymer melts only; it has been observed that they are also suited for an interpretation of the viscosities of concentrated solutions. Fujita and Kishimoto<sup>5</sup> assume the additivity of the fractional free volume of the polymer and solvent; they expressed the fractional free volume of the solution by the fractional free volume of pure polymer,  $f_2$ , and of pure solvent,  $f_1$ , according to the sizes of the volume fractions of the polymer,  $\varphi_2$ , and solvent,  $\varphi_1$ :

$$f = f_2\varphi_2 + f_1\varphi_1. \quad (2)$$

Besides the fractional free volume,  $f$ , the structure factor contained in the parameter  $A$  is also a function of concentration. It is directly proportional to the polymer concentration, so that if

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the reference viscosity is considered (with the parameters designated by an asterisk), it holds according to Fujita and Kishimoto

$$\eta/\eta^+ = (\varphi_2/\varphi_2^+) \exp [B(1/f - 1/f^+)] \quad (3)$$

The expression  $(\eta\varphi_2^+/\eta^+\varphi_2)$  is known as the concentration shift factor. The above relationship was used to attempt a graphic determination of the free volume parameters of pure components,  $f_1$  and  $f_2$ . Some authors regarded a solution with the highest concentration used<sup>5</sup> or melt<sup>6</sup> as the reference state, others used an infinitely dilute solution<sup>7</sup>. The magnitude of the constant  $B$  which is said to depend on the rigidity of the polymer chain and on the size and rigidity of the side substituents and is independent of the molecular weight and concentration of polymer varies between 1 and 2. It can be determined from the temperature dependence of the viscosity of the melt. For simplicity's sake the constant  $B$  was taken as unity in all determinations of  $f_2$  and  $f_1$ .

The objective of this work was a comparison of methods used for the determination of the free volume parameters in the extreme reference states  $\varphi_2^+ = 0$  and  $\varphi_2^+ = 1$  by using a single common system. No similar comparison has been carried out so far. For this purpose poly(dimethylsiloxane) was used as model polymer; it allowed a direct viscosity measurement by applying a single method (capillary viscometry) starting from very dilute solutions to a pure polymer.

## EXPERIMENTAL

The measurements were carried out with unfractionated samples of commercial poly(dimethylsiloxane), trade name Lukoil (Synthesia, Kolín, Czechoslovakia), the molecular weight of which was determined viscometrically (toluene, 25°C); the relationship<sup>8</sup>  $[\eta] = 8.28 \cdot 10^{-3} M_\eta^{0.72}$  was used for the calculations:

Sample:	<i>M</i> 50	<i>M</i> 100	<i>M</i> 200	<i>M</i> 350	<i>M</i> 500
$M_\eta$ :	5 700	10 400	15 800	21 900	24 100

Viscometers of the Ubbelohde type calibrated with sucrose solutions having a known viscosity were used for the measurements. For all five samples the dependence of viscosity on the concentrations of their solutions in a thermodynamically good solvent (toluene) and in the  $\theta$ -solvent (methyl ethyl ketone) was determined at 20°C within a concentration range  $\varphi_2$  of 0.05 to 1 (before measurements the solutions were filtered through glass fritted discs S 2). The density of solutions was determined pycnometrically.

## RESULTS AND DISCUSSION

The  $\eta$  vs  $\varphi_2$  dependence which is similar for all solutions is shown for the polymer *M* 200 in Fig. 1. If the pure polymer is the reference state ( $\varphi_2 = 1$ ), then according to Fujita and Maekawa<sup>6</sup> it holds for the concentration shift factor  $a_c = \eta/\eta^+(1 - \varphi_1)$ ; expression (3) becomes

$$-1/\ln a_c = f_2 + f_2^2/(f_1 - f_2)\varphi_1 \quad (4)$$

assuming that  $B = 1$ . The  $-1/\ln a_c$  vs  $\varphi_1^{-1}$  plot should be a straight line, and from the slope and the intercept it should be possible to calculate the fractional free volumes of the pure polymer and solvent. For our solutions in both toluene and methyl ethyl ketone the above dependences were represented by straight lines at concentrations higher than  $\varphi_2 \approx 0.2$ ; with decreasing concentration the plots became curved upwards with the exception of curves corresponding to the highest molecular weights (Fig. 2a,b). Contrariwise, Fujita and coworkers<sup>5,6</sup> give curves which are slightly bent downwards at lowest concentrations. The inappropriateness of Eq. (4) for low polymer concentrations is obvious at first glance because with decreasing concentration the shift factor increases *ad infinitum*. The cause should apparently be sought in that Doolittle's equation (1) originally derived for melts was also used for polymer solutions. This extension assumes solutions concentrated to such a degree that they exhibit a similar character of the macrostructure (formation of entanglements) and of the flow as the polymer melt. The effect of solvent viscosity which may be neglected for concentrated solutions gains in importance after passing to regions of lower concentrations, and the viscosity of the solvent as a contribution to the overall viscosity of the system cannot be neglected.

We tried to ascertain what curvature of the plot according to Eq. (4) follows from the theoretical expression of the viscosity of a dilute solution by means of the Huggins equation. According to the latter, the viscosity of a dilute solution is given by

$$\eta = \eta_s + [\eta] \eta_s c + k_H [\eta]^2 \eta_s c^2 ; \quad (5)$$

$\eta_s$  is viscosity of the solvent,  $[\eta]$  is intrinsic viscosity,  $k_H$  is interaction constant, and  $c$  is polymer concentration in g/dl.

$$a_c = [\eta_s/\varphi_2 + U[\eta] + k_H[\eta]^2 U^2 \varphi_2/\eta_2]/\eta^+ , \quad (6)$$

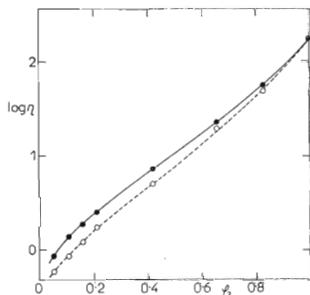


FIG. 1  
Dependence of Viscosity on Concentration  
of Solutions of Sample M 200  
In toluene (O) and in methyl ethyl ketone  
(●).

where  $U = 100\rho\eta_s$  and  $\rho$  is polymer density. It follows from Eq. (6) that the dependence  $-1/\ln a_c$  vs  $1/\varphi_1$  must pass through a minimum which will be shifted to lower values with increasing molecular weight. The minimum is given by

$$d(-1/\ln a_c)/d(1/\varphi_1) = (-\eta_s/\varphi_2^2 + k_H[\eta]^2 U^2/\eta_s)(1 - \varphi_2)^2/\eta^+ a_c \ln^2 a_c = 0 \quad (7)$$

and the corresponding polymer concentration reads

$$(\varphi_2)_{\min} = \eta_s/k_H^{1/2}U[\eta]. \quad (8)$$

With increasing molecular weight the intrinsic viscosity increases,  $(\varphi_2)_{\min}$  decreases, and consequently  $(\varphi_1^{-1})_{\min}$  decreases too. After substitution of the respective ex-

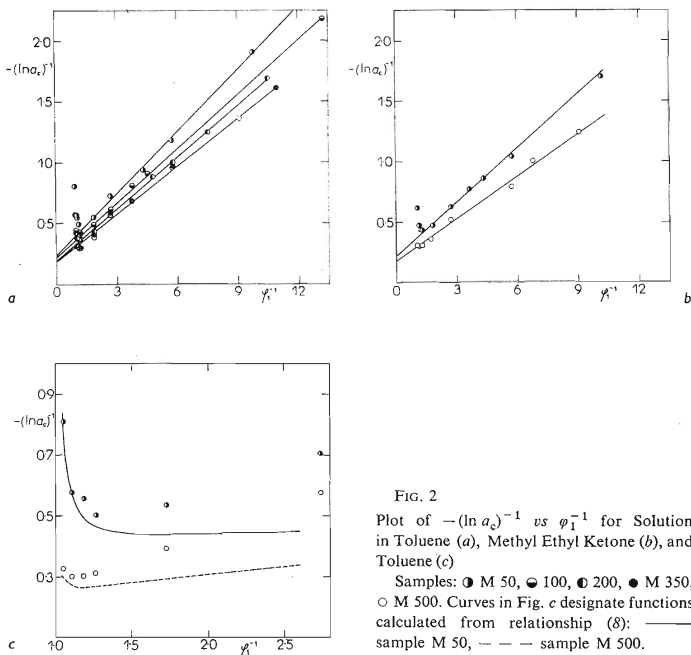


FIG. 2

Plot of  $-(\ln a_c)^{-1}$  vs  $\varphi_1^{-1}$  for Solution in Toluene (a), Methyl Ethyl Ketone (b), and Toluene (c)

Samples:  $\circ$  M 50,  $\bullet$  100,  $\bullet$  200,  $\bullet$  M 350,  $\circ$  M 500. Curves in Fig. c designate functions calculated from relationship (8): — sample M 50, - - - sample M 500.

perimental values  $[\eta] = 4.25 \cdot 10^{-2} \text{ dl/g}$ ,  $\eta^+ = 0.50 \text{ P}$ , and  $k_H = 0.32$  for a toluene solution of the sample M 50 and  $[\eta] = 11.9 \cdot 10^{-2} \text{ dl/g}$ ,  $\eta^+ = 4.30 \text{ P}$  for a solution of the sample M 500 into the derived function (6) we obtained a theoretical dependence of  $-1/\ln a_c$  vs  $\varphi_1^{-1}$  which in the low concentration region exhibits a course similar to our experimental results (Fig. 2c). For higher concentrations beyond the minimum the increase in the theoretical value of  $-1/\ln a_c$  is less steep than the experimental increase, which we regard as a consequence of neglecting higher interaction terms in the Huggins equation.

It can be seen from Fig. 2a that the intercept on the  $y$ -axis, *i.e.* the parameter  $f_2$ , slightly decreases with increasing molecular weight and the dependences for samples with the highest molecular weight (M 350 and M 500) practically coincide. By using the theoretical relationship derived by Williams, Landel, and Ferry<sup>9</sup>,  $f_2 = f_g + \alpha_f(T - T_g)$ , where  $f_g$  is the fractional free volume of the polymer at the glass transition temperature,  $\alpha_f$  is the expansion coefficient of the free volume,  $T$  is temperature and  $T_g$  is the glass transition temperature, and bearing in mind that only  $T_g$  depends perceptibly on molecular weight (with increasing molecular weight it increases to the limiting value), one can see that  $f_2$  thus expressed also decreases to a limiting value with increasing molecular weight.

Because of the small difference in intercepts on the  $y$ -axis and with respect to the possible inaccuracy in the plotting of straight lines through experimental points a quantitative expression of the dependence of experimental values of  $f_2$  on molecular weight is rather dubious. Consequently, there is even less reason in determining the parameter of the free volume of the solvent  $f_1 = f_2 + f_2^2/\gamma$ , which includes both squared error in  $f_2$  and an error in the slope of  $\gamma$ .

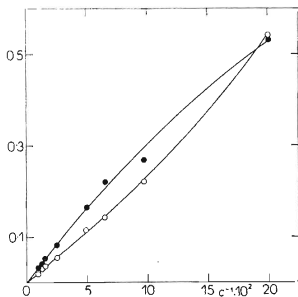


FIG. 3  
Plot of  $[\eta]/\ln(\eta_{sp}/c[\eta])$  vs  $c^{-1}$  for Solutions  
of Sample M 500

In toluene (●), and methyl ethyl ketone  
(○).

According to what is expected, an average value of  $f_2 = 0.21$  for the interval of the molecular weights used is virtually the same in both solvents. Owing to the different procedure of determination of both values and to a number of simplifying assumptions the accordance is comparatively good.

Another extreme alternative of the reference state is an infinitely dilute solution. In order to give the shift factor a real value also in an infinitely dilute solution, Rodriguez<sup>7</sup> somewhat arbitrarily replaced in Eq. (3) the absolute viscosity by the specific viscosity. We believe that the same result may be attained with more accuracy from a theoretically calculated relationship describing the behaviour of the model of a polymer coil, *e.g.*, represented by chains of spheres connected by elastic springs moving in a medium having the viscosity  $\eta_s$ . The contribution of the polymer viscosity to the solution viscosity is given by the first term in the equation

$$\eta = (N/6) (\overline{s_0^2}/M) Z \varphi_2 \zeta + \eta_s, \quad (9)$$

where  $N$  denotes the Avogadro number,  $(\overline{s_0^2})^{1/2}$  is the radius of gyration of an unperturbed polymer coil,  $M$  is molecular weight, and  $Z$  is the number of atoms in the backbone of a polymer chain. The frictional coefficient per chain atom is proportional to the viscosity of the medium  $\zeta = \zeta' \eta_s$ ,  $\zeta'$  being an exponential function of the term  $B/f$  in Doolittle's equation. Expression (9) then assumes a form in which specific viscosity is the function of molecular parameters or concentration

$$(\eta - \eta_s)/\eta_s = \eta_{sp} = (N/6) (\overline{s_0^2}/M) Z \varphi_2 \zeta'. \quad (10)$$

The fraction  $\eta/(1 - \varphi_1)$  then becomes an expression proportional to reduced viscosity  $100\varrho(\eta_{sp}/c)$ ,  $\eta^+/(1 - \varphi_1^+)$  becomes an expression proportional to intrinsic viscosity  $100\varrho[\eta]$ , and the concentration frictional factor is given by  $a_c = \eta_{sp}/c[\eta]$ . By rearranging Eq. (3), we obtain

$$\ln a_c = c(f_1 - f_2)f_1^2[100\varrho - c(f_1 - f_2)/f_1], \quad (11)$$

relationship similar to the empirical equation of Lyons and Tobolsky<sup>10</sup>

$$\ln (\eta_{sp}/c[\eta]) = k_H c[\eta]/(1 - bc), \quad (12)$$

where  $b$  is a constant independent of concentration and varying according to the polymer-solvent system. By comparing both relationships we have  $f_1 = b/k_H[\eta]$  and  $f_2 = f_1(1 - 100\varrho b)$ .

Eq. (12) was rearranged by Rodriguez to become

$$[\eta]/\ln (\eta_{sp}/c[\eta]) = 1/k_H c - b/k_H; \quad (13)$$

according to the above equation, the plot  $[\eta]/\ln(\eta_{sp}/c[\eta])$  vs  $1/c$  should be linear, with the slope  $1/k_H$  and the intercept on the  $y$ -axis  $-b/k_H$ . Fig. 3 shows that the dependences obtained for a solution in toluene and methyl ethyl ketone are somewhat curved, the character of the curvature being different for both solvents. One of the causes of such curvature may consist in a not completely exact reference value of intrinsic viscosity.

In the extrapolation to zero value the  $1/c$  curves seem to go to the beginning. If the parameter  $b$  is calculated by using (12) from intrinsic viscosity, interaction constant  $k_H$  and solution viscosity for a number of various concentrations, the values thus obtained differ more than tenfold within the whole concentration interval, so that their use for direct calculation of the parameters  $f_1$  and  $f_2$  has no sense. It can be seen from them, however, that  $b$  has a very low absolute value ( $10^{-3}$  to  $10^{-4}$ ), and the fraction  $b/k_H$  in Fig. 3 as an intercept on the  $y$ -axis cannot be distinguished from zero. Consequently, a method based on equation (13), i.e. the plot  $[\eta]/\ln(\eta_{sp}/c[\eta])$  vs  $1/c$  is not suited for the determination of the free volume parameters.

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