An equation suitable for describing the viscosity of dilute to moderately concentrated polymer solutions*

R. F. Fedors
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91103, USA
(Received 7 April 1978; revised 8 August 1978)

It is shown that an equation first derived for describing the Newtonian viscosity of suspensions of rigid spheres is also applicable for describing the Newtonian viscosity of dilute to moderately concentrated polymer solutions. The equation is applicable for relative viscosities from 1 to about 100. In addition, it is possible to rearrange the equation so that the intrinsic viscosity is expressible as an explicit function of the other variables. This leads to a very convenient method of calculating the intrinsic viscosity from a determination of the relative viscosity at a single polymer concentration.

INTRODUCTION

Equations exist which can sometimes describe the viscosity of polymer solutions over the whole concentration range. One of these is the two parameter Martin equation[1], which is given by:

$$\ln \frac{\eta_{sp}}{c} = \ln[\eta] + K[\eta]c \qquad (1)$$

where η_{sp} is the specific viscosity, c is the concentration of polymer in g/dl, $[\eta]$ is the intrinsic viscosity and K is a parameter. Another is the Lyons and Tobolsky[2] expression:

$$\ln \frac{\eta_{sp}}{c[\eta]} = \frac{k_1[\eta]c}{1-bc} \qquad (2)$$

where k_1 and b are parameters. When $b = 0$, equation (2) reduces to equation (1). From a knowledge of K in the case of equation (1) or k_1 and b in the case of equation (2) for a given polymer–solvent system, the equations can be used to estimate the intrinsic viscosity from a determination of the relative viscosity η_r at a single concentration. One drawback to both equations (1) and (2) is that they cannot be written in a form such that $[\eta]$ is an explicit function of the remaining variables. Hence, it is usual to estimate $[\eta]$ by the method of successive approximation. However, Rodriguez[3] has recently constructed a nomograph for the Martin equation whereby approximate estimates of $[\eta]$ can be quickly obtained: however, for precise values, successive approximations must still be employed.

DISCUSSION

Viscosity of dilute to moderately concentrated polymer solutions

We have found that an equation proposed by van Dijck[4] and first applied to the viscosity of Newtonian suspensions of rigid particles by Eilers can also be used to describe the viscosity of dilute to moderately concentrated polymer solutions. In addition, the equation can be rearranged so that $[\eta]$ becomes an explicit function of polymer concentrations. The same equation has been shown to describe the relative modulus–filler content relationship of filled elastomers[5–7] and to describe the dependence of viscosity on concentration for aqueous electrolyte solutions[8]. The equation is given by:

$$\eta_r = \left(1 + \frac{1.25\,\phi}{1 - \phi/\phi_m}\right)^2 \qquad (3)$$

where ϕ is the volume fraction of suspended particles and ϕ_m is the maximum volume fraction to which the particles can pack. For large rigid suspended particles, the value of ϕ_m can be independently estimated from sedimentation experiments. If it is assumed that ϕ is proportional to the polymer concentration, then:

$$\phi = kc \qquad (4)$$

where k is the constant of proportionality. Hence,

$$\eta_r = \left(1 + \frac{1.25\,kc}{1 - \dfrac{c}{c_m}}\right)^2 \qquad (5)$$

---

* This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS7-100, sponsored by the National Aeronautics and Space Administration

0032–3861/79/020225–04$02.00

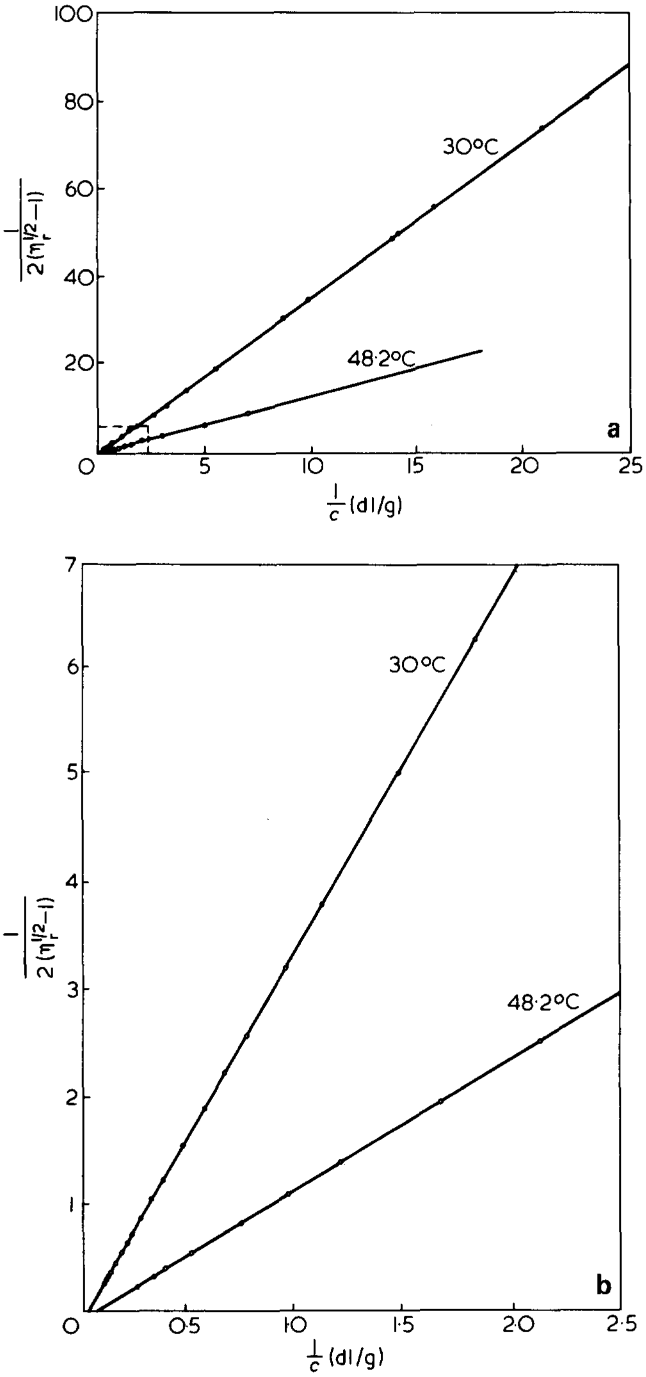

Figure 1 Plot of viscosity data in the form suggested by equation (7). Polystyrene MW = 1.46 x 10^5 gm/moles in toluene at 30° C (filled circles) and at 48.2° C. Part (a) represents the entire concentration range while part (b) represents the dilute range. Data from reference 7

where c_m is a polymer concentration parameter (the hydrodynamic spheres considered to be rigid) which corresponds to ϕ_m. For small c, equation (5) reduces to $\eta_r = 1 + 2.5\,kc$ and hence, $2.5\,k = [\eta]$. Using this result:

$$\eta_r = \left[1 + \frac{[\eta]c}{2\left(1 - \dfrac{c}{c_m}\right)}\right]^2 \qquad (6)$$

which contains the two parameters $[\eta]$ and c_m.

For purposes of testing this expression, it is convenient to rearrange it to the form:

$$\frac{1}{2(\eta_r^{1/2} - 1)} = \frac{1}{[\eta]c} - \frac{1}{[\eta]c_m} \qquad (7)$$

and hence a plot of the quantity $1/2(\eta_r^{1/2} - 1)$ *versus* $1/c$ should result in a linear response with slope equal to $1/[\eta]$ and intercept $1/[\eta]c_m$. Contrary to the behaviour of equations (1) and (2), equation (7) can be rearranged to yield $[\eta]$ explicitly:

$$[\eta] = 2(\eta_r^{1/2} - 1)(1/c - 1/c_m) \qquad (8)$$

and hence, once the value of c_m has been established for a given polymer–solvent system, $[\eta]$ can easily be calculated from a determination of η_r at a single polymer concentration.

We have examined a great deal of viscosity–concentration data for various polymer–solvent systems and find that equation (7) is generally applicable for η_r values from 1 to about 100. For purposes of demonstration, we will use the viscosity data of Weissberg, Simha, and Rothman for dilute and moderately concentrated solutions of polystyrene at three molecular weight levels and for several solvents and temperatures[9].

Figure 1a shows the data for a fraction of molecular weight 1.46 x 10^5 g/mol in toluene at 30° and at 48.2°C. As may be seen, the response is quite linear. *Figure 1a* shows the data over the entire concentration range while the data points contained in the small rectangle and representing the dilute range are shown in *Figure 1b*. Equation (7) is very sensitive to the values of η_r in the dilute range, i.e. for c values less than about 1 g/dl, because the quantity $1/2(\eta_r^{1/2} - 1)$ approaches infinity as c tends to zero. In this region, small variations in η_r can produce large changes in $1/2(\eta_r^{1/2} - 1)$. In our experience, we generally apply equation (7) to the data by omitting the data in the very dilute range and fit the remaining data using a least squares fitting technique.

Figure 2 shows the same data as in *Figure 1* fitted to the Martin equation. It is apparent that the data in the dilute range deviate somewhat from a linear response. The results obtained by fitting both the Martin equation and equation (7) to the viscosity data for polystyrene reported by Weissberg *et al.*[9] are summarized in *Table 1*. Columns 4 and 5 list the least squares estimates for the slope and intercept, respectively, for equation (7) while columns 6 and 7 list the respective quantities obtained using Martin's equation. Equation (7) provided estimates of η_r for all the data given by Weissberg *et al.* with an average deviation of 0.67% compared to the experimentally measured values of η_r, while the Martin equation provided estimates of η_r with an average deviation of 0.72%.

In column 8 are shown the values of $[\eta]$ reported by Weissberg *et al.*: in column 9 the corresponding value obtained from the slope using equation (7) is given, while column 10 lists the value obtained from the Martin equation. The average deviation in $[\eta]$ obtained using equation (7) is 4.8% while that obtained using Martin's equation is 5.1%.

Column 11 lists the values of the parameter c_m obtained from equation (7). As noted previously, c_m should be proportional to ϕ_m the maximum volume fraction to which rigid particles can pack. Scott[10] has shown, using large monodisperse spheres such as ball bearings, that $\phi_m = 0.63$. When the spheres are polydisperse, ϕ_m will have a higher value because smaller spheres are sometimes able to fit into the interstitial spaces associated with the larger particle. The upper limiting value of ϕ_m for rigid spheres is unity. The values of ϕ_m calculated from equation (7) are also listed in *Table 1*, and, as may be seen, are all greater than unity.

Since ϕ_m values greater than unity are not possible for systems which contain rigid particles, the fact that polymeric systems such as described herein lead to ϕ_m values varying from 2 to about 10 is not explicable at this time; however, it is felt that these high ϕ_m are in some way related to the fact that the highly swollen polymer coils are deformable. In view of this, we take ϕ_m for polymer systems to be an empirical fitting parameter.

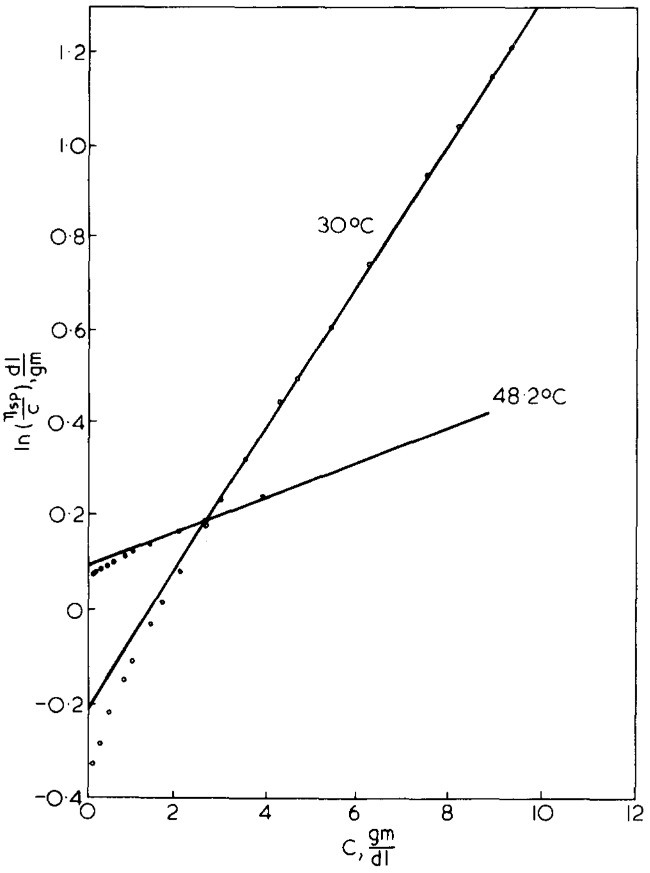

Figure 2 Same data as in figure plotted in the form suggested by the Martin equation

Viscosity and reduced variables

If we expand the square term on the right hand side of equation (6) the following equation can be derived:

$$\frac{\eta_{sp}}{[\eta]c} = \frac{1}{\left(1 - \frac{c}{c_m}\right)} + \frac{\frac{c_m[\eta]}{4}\,\frac{c}{c_m}}{\left(1 - \frac{c}{c_m}\right)^2} \tag{9}$$

which shows that the fraction $\eta_{sp}/[\eta]\,c$ is a function of the reduced variable c/c_m. For polymer–solvent systems in which $c_m\,[\eta]\,/4$ is relatively constant (as, for example, when only the molecular weight of the polymer is varied) a plot of $\eta_{sp}/[\eta]\,c$ *versus* c should be superposable by a simple horizontal shift along the c-axis. Utracki and Simha have shown that this is indeed the case in that different polymer–solvent systems gave responses which had similar, and, in some cases, wholly superposable responses[11]. In fact, the dependence of the ratio $\eta_{sp}/[\eta]\,c$ on c is the basis of their treatment of the viscosity of dilute to concentrated polymer solutions in terms of reduced variables. Equation (9) predicts that this should indeed be the case, at least for dilute to moderately concentrated polymer solutions.

REFERENCES

1 Martin, A. F., *Am. Chem. Soc. Meeting, Memphis,* April 1942; Davis, W. E. and Elliott, J. H. in 'Cellulose and Cellulose Derivatives', Part III, (Eds. E. Ott., H. Spurlin and J. H. Elliott) Interscience, New York, 1955, p 1216
2 Lyons, P. R. and Tobolsky, A. V. *Polym. Eng. Sci.* **1970, 10,** 1
3 Rodriguez, F. *J. Polym. Sci. (B)*1973, **11,** 485
4 Eilers, H. *Kolloid Z.* 1944, **97,** 313
5 Fedors, R. F. *Polymer* 1978, **19**
6 Landel, R. F. and Smith, T. L. *Am. Rocket Soc. J.* 1960, **31,** 599

Table 1

1 Temperature (°C)	2 Solvent	3 *MW* x 10^5 g/mol	4 Slope (equation 7)	5 Intercept (equation 7)	6 Slope (equation 1)	7 Intercept (equation 1)	8 $[\eta]$ (ref 9)	9 $[\eta]$ (equation 7)	10 $[\eta]$ (equation 1)	11 c_m	12 ϕ_m
30.0	Toluene	6	0.4740	−0.0373	0.4632	0.7898	2.041	2.110	2.203	12.71	10.7
48.2	Toluene	6	0.4956	−0.0373	0.4356	0.7561	1.968	2,012	2.130	13.33	10.7
30	MEK	6	0.8988	−0.0885	0.3852	0.0936	1.020	1.113	1.098	10.15	4.52
48.2	MEK	6	0.9096	−0.0883	0.3841	0.0747	0.9771	1.099	1.078	10.30	4.53
30	0.9 MEK/	6	1.1867	−0.1674	0.4147	−0.2157	0.7709	0.8427	0.8060	7.05	2.38
48.2	0.1 propyl alcohol	6	1.1664	−0.1552	0.4012	−0.1926	0.8740	0.8573	0.8248	7.52	2.58
30	Toluene	1.46	1.3726	−0.0402	0.1576	−0.2364	0.7050	0.7285	0.7895	34.2	9.97
48.2	Toluene	1.46	1.5865	−0.0387	0.1439	−0.4406	0.6190	0.6303	0.6437	41.0	10.3
30	MEK	1.46	2.1985	−0.0982	0.1652	−0.8059	0.4454	0.4549	0.4467	22.4	4.08
48.2	MEK	1.46	2.5161	−0.1075	0.1527	−0.9565	0.3870	0.3974	0.3842	23.4	3.72
30	0.9 MEK/	1.46	2.8665	−0.1277	0.1539	−1.1208	0.3207	0.3489	0.3260	22.4	3.13
48.2	0.1 propyl alcohol	1.46	2.7903	−0.1197	0.1533	−1.1004	0.3509	0.3584	0.3327	23.3	3.34
30	Toluene	0.58	2.6584	− 0.0489	0.1060	−0.9898	0.3689	0.3762	0.3717	54.4	8.19
48.2	Toluene	0.58	2.9199	−0.0526	0.1053	−1.1040	0.3231	0.3425	0.3315	55.5	7.60

7 Landel, R. F. in 'Mechanics and Chemistry of Solid Propellants', (Eds. Liebowitz Roh and Crowley) Pergamon Press, New York, 1966

8 Fedors, R. F., unpublished results

9 Weissberg, S. G., Simha, R. and Rothman, S. *J. Res. Nat. Bur. Stand.* 1951, **47**, 298

10 Scott, G. O. *Nature* 1960, **188**, 908

11 Utracki, L. and Simha, R. *J. Polym. Sci. (A)* 1963, **1**, 1089