Viscosity of dilute to moderately concentrated polymer solutions

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An equation suggested by Fedors for application to intrinsic viscosity determination of dilute to moderately concentrated solutions is re-examined taking into account polymer swelling behaviour and polymer–solvent interactions. For a given polymer–solvent system, the observed variation of the constant of the equation (defined as the maximum volume fraction to which polymer particles can pack), ϕ_m, and its estimated values beyond its theoretical limit of unity are the main difficulties in its application. These problems are solved by a suggested modification to the equation, and ϕ_m is shown to be less than or equal to unity and constant for many polymer–solvent systems. This modification facilitates the use of the Fedors equation for dilute to concentrated polymer solutions for determining the intrinsic viscosity at a single polymer concentration.

(Keywords: intrinsic viscosity; Fedors equation; volume fraction; molecular aggregation; goodness of solvent)

INTRODUCTION

The intrinsic viscosity of a polymer solution is usually determined by Huggins' equation for dilute solutions (concentrations below 1% w/v); and for moderate concentrations (>1%), Martin's equation is the most preferred equation, among many such equations suggested in the literature.

Huggins' equation for low concentration:

$$\eta_{sp/C} = [\eta] + K_H[\eta]^2 C \qquad (1)$$

where K_H is Huggins' coefficient, $\eta_{sp} = (\eta - \eta_0)/\eta_0$ (η and η_0 being viscosity of polymer solution and solvent respectively), and C is polymer concentration.

Martin's equation for moderate concentration:

$$\ln \eta_{sp/C} = \ln[\eta] + K_M[\eta]C \qquad (2)$$

where K_M is Martin's coefficient.

From knowledge of K_H or K_M, equations (1) and (2) can be used to determine the intrinsic viscosity $[\eta]$ at a single concentration. The main drawback of these equations (equation (2) in particular) is that they cannot be rearranged to a form such that $[\eta]$ is an explicit function of the remaining variables. Successive approximation methods are therefore employed to have a quick approximate estimate of $[\eta]$.

Fedors[1,2] found that the equation developed and applied to viscosities of aqueous suspensions can be used to fit a wide variety of experimental data. This equation relates volume fraction of particles in suspension to the relative viscosity by:

$$\eta_r = (1 + 1.25\phi_{eff})^2 \qquad (3)$$

where ϕ_{eff} is the effective volume fraction of particles:

$$\phi_{eff} = \frac{\phi}{1 - \phi/\phi_m} \qquad (4)$$

where ϕ_m is the maximum volume fraction to which particles can pack, and ϕ is the actual volume fraction of particles in the suspension.

Assuming $\phi = KC$, where K is a constant of proportionality and C is polymer concentration, Fedors[1] derived an expression for relative viscosity as a function of concentration using equations (3) and (4):

$$\eta_r = \left(1 + \frac{1.25KC}{1 - C/C_m}\right)^2 \qquad (5)$$

Unlike equations (1) and (2), equation (5) can be rearranged to yield explicitly:

$$[\eta] = 2(\eta_r^{1/2} - 1)(1/C - 1/C_m) \qquad (6)$$

Equation (6) can be used for determining $[\eta]$ by measuring relative viscosity at a single concentration knowing the value of C_m, established *a priori*, for a given polymer–solvent system.

Fedors applied[1] equation (6) to the viscosity data on polystyrene, in the range of dilute to moderate concentrations, for different molecular weights, solvents and temperatures. Equation (6) was shown to give a better fit over the whole concentration range than Martin's equation.

Is is shown that for rigid monodisperse spheres such as ball-bearings $\phi_m = 0.63$, and for polydisperse materials ϕ_m values calculated by Fedors for polystyrene were found to vary between 2 to about 10. Fedors considered ϕ_m as only an empirical fitting parameter since values of ϕ_m greater than unity cannot be explained satisfactorily. Ioan *et al.*[3] later applied equation (6) to their data on poly(butyl methacrylate) of various molecular weights in methyl ethyl ketone (MEK) at 25°C. They also obtained ϕ_m values greater than unity and ranging from 7 to 10 for the same polymer–solvent system but with varying molecular weights.

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A modification to equation (6) is suggested in this paper, taking into account the solvent–polymer interaction effects. The modified equation gave values of ϕ_m less than or equal to unity in a wide variety of polymers, and they also remained constant for a given polymer–solvent system.

VISCOSITY MEASUREMENTS

Some of the viscosity data used here have been taken from literature[1,3–6]. In addition, we have measured the viscosity of polyester and nylon at different concentrations using an Ubbelohde viscometer at 20 ± 0.01°C. The flow times of solvents used was above 100 s. Kinetic energy corrections were found to be negligible. The flow volume is greater than 5 ml, minimizing drainage errors. For nylon we used 96% H_2SO_4 and for polyester we used 60/40 phenol/tetrachloroethane (TCE) as solvents. The concentration range was 1×10^{-3} to 2×10^{-2} g cm^{-3}.

Polyester materials used are apparel-grade granules ($IV \approx 0.60$) and technical-grade granules ($IV \approx 0.90$). Nylon materials used are tyrecord-grade granules ($RV \approx 3.3$ in 96% H_2SO_4).

DISCUSSION

The effective volume in equation (6) is originally derived[2] from:

$$\phi_{\mathrm{eff}} = \frac{V_p}{V_t - V_0} = \frac{\phi}{1 - \phi/\phi_m} \tag{7}$$

where

$$\phi = V_p/V_t \qquad \phi_m = V_p/V_0 \tag{8}$$

V_p is the volume of the particles (equal to the weight of the particles divided by the true density), V_t is total volume of the suspension and V_0 is the void volume of aggretates formed by particle-to-particle adhesion. This is based on the principle[2] that a fraction of fluid is immobilized in the interstitial space within the aggregates and not available for flow. ϕ_m is the maximum volume fraction to which the suspended particles can pack. For rigid particles, which are not substantially affected by swelling by the solvent, these simple relationships given by (7) and (8) hold good and the volume fraction ϕ will be less than unity. However, for polymer dissolved in solutions, hydrodynamic theories predict that the volume fraction of polymer is affected by swelling of polymer coils due to polymer–solvent interaction. The higher this interaction, the greater are the swelling effects. Taking this swelling factor into account, the volume fraction ϕ of swollen polymer particles is given by:

$$\phi = C\varepsilon_0/\rho \tag{9}$$

where ε_0 is the swelling factor. For dilute to moderate concentrations ε_0 can be obtained from:

$$\varepsilon_0 = [\eta]\rho/2.5 \tag{10}$$

where ρ is the density of dry polymer and $[\eta]$ is the intrinsic viscosity of the polymer.

Hence ϕ is given by:

$$\phi = [\eta]C/2.5 \tag{11}$$

From this, it can be seen that ϕ exceeds unity at concentrations greater than $2.5/[\eta]$. For a polymer having an intrinsic viscosity less than 2.5, ϕ values exceed unity even at concentrations less than 1%. The denominator in equation (4), i.e. $1 - \phi/\phi_m$, can give rise to the absurdity of negative effective volume fractions if ϕ_m is less than or equal to unity while ϕ is greater than unity. The experimental data therefore result in ϕ_m greater than unity while equation (6) is fitted to them, which was the case with reported values[1,3] of ϕ_m. The fact that equation (6) gives a good fit despite the above theoretical limiting values of ϕ_m indicates that some other factor is missing in the assumptions made in the derivation of this expression.

In viscosity measurements the volume of the solvent (V_s) is taken as equal to 1 dl (100 ml) and the concentration of polymer in the solvent is expressed in grams per decilitre. The total volume of the polymer–solvent (V_t) can be expressed as:

$$V_t = V_p + V_s = V_p + 1 \tag{12}$$

The true volume fraction (ϕ_t) of polymer in the suspension is then given by:

$$\phi_t = V_p/V_t = V_p/(V_p + 1) \tag{13}$$

The volume fraction measured in terms of concentration in relative viscosity measurements is not the true volume fraction because it is taken as V_p/V_s, which is valid only under the condition that $V_p \ll V_s$. As V_s is unity and V_p often exceeds unity owing to polymer particle swelling, the contribution of polymer volume to total volume cannot be ignored in taking volume fractions.

The apparent volume fraction (ϕ_a) measured is given by:

$$\phi_a = V_p/V_s = V_p \qquad (\text{as } V_s = 1) \tag{14}$$

and also

$$\phi_a = (C/\rho)\varepsilon_0 = [\eta]C/2.5 \tag{15}$$

Substituting equation (14) in (13) gives the true volume fraction:

$$\phi_t = \phi_a/(1 + \phi_a) \tag{16}$$

When the volume fraction ϕ in equation (14) is taken as the true volume fraction ϕ_t, it can be modified as:

$$\phi_{\mathrm{eff}} = \frac{\phi_t}{1 - \phi_t/\phi_m} \tag{17}$$

Therefore

$$\phi_{\mathrm{eff}} = \frac{\phi_a/(1 + \phi_a)}{1 - [\phi_a/(1 + \phi_a)](1/\phi_m)} \tag{18}$$

or

$$\phi_{\mathrm{eff}} = \frac{\phi_a}{1 + \phi_a - (\phi_a/\phi_m)} \tag{19}$$

Substituting equations (19) and (15) in equation (3), the relative viscosity is given by:

$$\eta_r = \left(1 + \frac{[\eta]C/2}{1 - ([\eta]C/2.5)(1/\phi_m)}\right)^2 \tag{20}$$

Rearranging equation (20) gives:

$$\frac{1}{2(\eta_r^{1/2} - 1)} = \frac{1}{[\eta]C} - \frac{(a - 1)}{2.5}$$

where $a = 1/\phi_m$. When $2(\eta_r^{1/2} - 1)^{-1}$ is plotted as a function of reciprocal of concentration (g dl^{-1}), the slope

Table 1 Viscosity data[1] for polystyrene samples in different solvents

M_w ($\times 10^5$ g mol^{-1})	Solvent	Temperature (°C)	$[\eta]$ (dl g^{-1}) (ref. 1)	Slope (ref. 1)	ϕ_m (ref. 1)	ϕ_m (eqn (20))
0.58	Toluene	30	0.3717	−0.0489	8.19	0.89
1.46			0.7895	−0.0402	9.97	0.91
6.0			2.110	−0.0373	10.7	0.91
0.58	Toluene	48.2	0.3315	−0.0526	7.60	0.88
1.46			0.6303	−0.0387	10.3	0.91
6.0			2.012	−0.0373	10.7	0.91
1.46	MEK	30	0.4549	−0.0982	4.08	0.80
6.0			1.1130	−0.0885	4.52	0.82
1.46	MEK	48.2	0.3974	−0.1075	3.72	0.79
6.0			1.099	−0.0883	4.53	0.82
1.46	0.9 MEK/0.1 propyl alcohol[a]	30	0.3489	−0.1277	3.13	0.76
6.0			0.8427	−0.1674	2.38	0.70
1.46	0.9 MEK/0.1 propyl alcohol	48.2	0.3584	−0.1197	3.34	0.77
6.0			0.8573	−0.1552	3.58	0.72

[a] For this solvent–polymer system ϕ_m shows some dependence on molecular weight

Table 2 Viscosity data[3] for poly(butyl methacrylate) samples in MEK at 25°C

Sample	$[\eta]$ (dl g^{-1}) (ref. 3)	C_m (g dl^{-1}) (ref. 3)	ϕ_m (ref. 3)	ϕ_m (eqn (20))
1	7.25	3.63	10.59	0.91
2	8.87	2.25	8.00	0.89
3	10.28	2.43	9.99	0.91
4	10.55	2.37	10.00	0.91
5	10.84	2.31	10.03	0.91
6	11.43	1.61	7.28	0.88
7	11.65	1.83	8.53	0.90

yields the intrinsic viscosity $[\eta]$ and the intercept gives the value of a and consequently ϕ_m.

Applying equation (20) to the data on slopes and intercepts given by Fedors[1] and Ioan *et al.*[3], ϕ_m values are calculated and compared with the values obtained using equation (6) in *Tables 1* and *2*. It is evident that ϕ_m values obtained applying equation (20) are always less than unity and more or less constant in some of the polymer–solvent systems.

Further, we have applied equation (20) to viscosity data given by Hager *et al.*[5] for polystyrene in θ temperature conditions and to viscosity data given by Nagy *et al.*[4] for poly(vinyl chloride). In addition to this, the viscosity data obtained in this laboratory for low- and high-molecular-weight poly(ethylene terephthalate) were also fitted by equation (20) to get $[\eta]$ and ϕ_m values. The data thus obtained are shown in *Figures 1* and *2* and also tabulated in *Tables 3* and *4*. For comparison, the Huggins' coefficient is also given as obtained by applying equation (1) to data of poly(vinyl chloride) and polyester samples for which the concentration is in the dilute range. It is interesting to note that a polymer–solvent system having lower K_H tends to give higher values of ϕ_m.

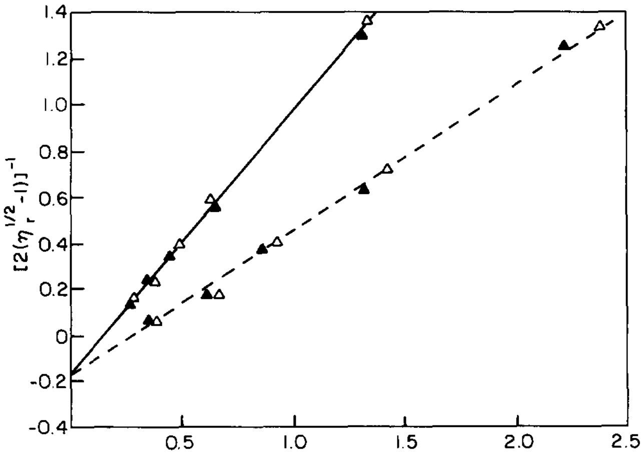

Figure 1 Plot of $[2(\eta_r^{1/2}-1)]^{-1}$ vs. $1/C$ for polystyrene samples: (——) for $M_w = 8.62 \times 10^5$; (– – –) for $M_w = 2.0 \times 10^6$; (▲) viscosity data in cyclopentane at $\theta_L = 19.5$°C; (△) viscosity data in cyclopentane at $\theta_U = 143.5$°C. (Data from ref. 5)

Value of ϕ_m and goodness of solvents

One of the important consequences of equation (19) is that when ϕ_m is near to or equal to unity:

$$\phi_{eff} \approx \phi_a \qquad (21)$$

and under these conditions equation (3) can be reduced to equation (1) with K_H taken as 0.25:

$$\begin{aligned}\eta_r &= (1 + 1.25\phi_{eff})^2 \\ &= (1 + 1.25\phi_a)^2 \\ &= 1 + \frac{2.5[\eta]C}{2.5} + \frac{[\eta]^2C^2}{4} \\ &= 1 + [\eta]C + 0.25[\eta]^2C^2\end{aligned}$$

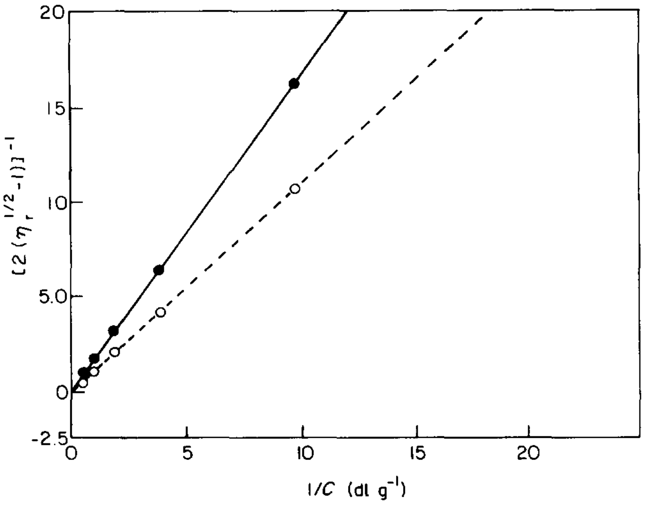

Figure 2 Plot of $[2(\eta_r^{1/2}-1)]^{-1}$ vs. $1/C$ for polyester samples in dilute solution in 60/40 phenol/TCE at 20°C: (——) for apparel-grade polyester ($M_w \approx 37\,000$); (---) for technical-grade polyester ($M_w \approx 67\,000$)

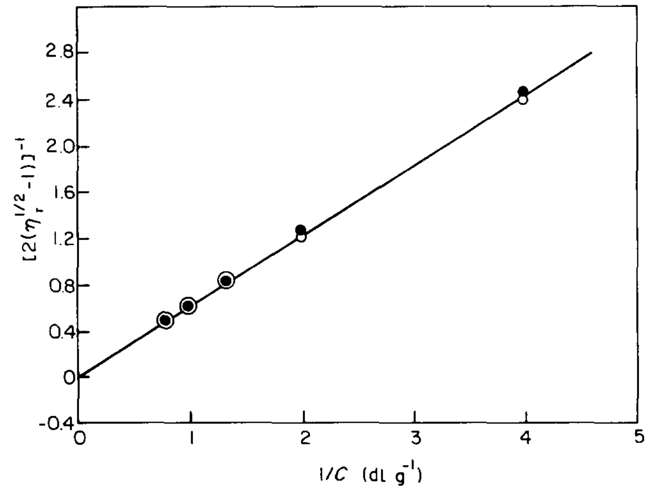

Figure 3 Plot of $[2(\eta_r^{1/2}-1)]^{-1}$ vs. $1/C$ for nylon-6 (tyrecord grade) in dilute solution in 96% H_2SO_4 at 20°C: (●) fresh dried nylon-6 tyrecord-grade granules; (○) nylon-6 tyrecord-grade granules stored for 5 months in N_2 atmosphere. Data points for yarn could not be given due to overlap

Table 3 Viscosity data for polystyrene at θ conditions[5] and poly(vinyl chloride) in dilute conditions[4]

Sample	Molecular weight (g mol^{-1})	Solvent	Temperature (°C)	$[\eta]$ (dl g^{-1}) (eqn (20))	Intercept (eqn (20))	ϕ_m
Polystyrene	8.62×10^5	Cyclopentane	19.5	0.911	−0.1688	0.70
			154.5	0.906	−0.1623	0.71
	2.0×10^6	Cyclopentane	19.5	1.577	−0.1743	0.70
			154.5	1.575	−0.1843	0.68
Poly(vinyl chloride)	0.97×10^5	Tetrahydrofuran	25	1.001	−0.2632	0.60

Table 4 Viscosity data of polyester samples in dilute solutions of 60/40 phenol/TCE at 20°C

Sample	$[\eta]$ (dl g^{-1}) (eqn (1))	K_H (eqn (1))	$[\eta]$ (dl g^{-1}) (eqn (20))	Intercept (eqn (20))	ϕ_m
Apparel-grade granules ($M_w \approx 0.37 \times 10^5$)	0.620	0.33	0.611	−0.1036	0.79
Technical-grade granules ($M_w \approx 0.67 \times 10^5$)	0.945	0.32	0.923	−0.0994	0.80
	0.911	0.36	0.904	−0.0962	0.81
	0.940	0.36	0.932	−0.1063	0.79
POY ($M_w \approx 0.35 \times 10^5$)	0.598	0.44	0.601	−0.1533	0.72

Table 5 Viscosity data for nylon-6 technical-grade polymer with $M_w \approx 0.56 \times 10^5$ g mol^{-1} in 96% H_2SO_4 at 20°C

Sample details	$[\eta]$ (dl g^{-1}) (eqn (1))	K_H (eqn (1))	$[\eta]$ (dl g^{-1}) (eqn (20))	Interceprt (eqn (20))	ϕ_m
Dry granules fresh from production	1.623	0.26	1.633	−0.0015	0.997
Dry granules stored for 5 months	1.663	0.26	1.666	−0.0016	0.996
Tyrecord yarn	1.583	0.26	1.572	−0.0094	0.977

Table 6 Viscosity data[6] of polyester (POY) yarn in different compositions of phenol/TCE mixtures at 25°C

Composition of phenol/TCE	$[\eta]$ (dl g^{-1})^a (ref. 6)	K_H (ref. 6)	$[\eta]$ (dl g^{-1})^a (eqn (20))	Intercept (eqn (20))	ϕ_m
15/85	0.554 ($r = 0.994$)	0.79	0.590 ($r = 0.999$)	−0.2297	0.63
30/70	0.482 ($r = 0.991$)	1.62	0.540 ($r = 0.999$)	−0.5045	0.44
50/50	0.413 ($r = 0.985$)	2.51	0.510 ($r = 0.999$)	−0.5495	0.42
70/30	0.312 ($r = 0.972$)	3.34	0.385 ($r = 0.999$)	−0.8197	0.33

[a] The values given in parentheses are linear regression correlation coefficients (r)

i.e.

$$\eta_{sp}/C = [\eta] + 0.25[\eta]^2C^2 \qquad (22)$$

This means that for those polymer–solvent systems having $K_H = 0.25$ the value of ϕ_m should be near to or equal to unity. This is possible only in dilute solutions and good solvents. From our viscosity data on nylon-6 in dilute conditions, we noted that K_H is always near 0.25, when viscosity is measured in 96% H_2SO_4. When we used the same viscosity data to fit equation (2), the ϕ_m values were indeed found to be near unity, as shown in *Figure 3* and *Table 5*. Thus ϕ_m can be taken as a good measure of goodness of solvents.

Value of ϕ_m and molecular aggregation

Under certain experimental conditions, such as, for example, viscosity measurements in mixed solvents, with one of the components varied from 0 to 100%, the intrinsic viscosity and Huggins' coefficient are drastically affected owing to increased polymer-to-polymer interaction *vis-à-vis* the polymer-to-solvent interaction. In such cases, polymer particles tend to adhere to each other and form larger and larger aggregrates. The Huggins' coefficient is found to be higher than unity in such cases[6]. To see how ϕ_m values are affected in such cases, we have fitted equation (20) to the viscosity data on polyester (POY) yarn measured in different combinations of phenol/TCE solutions as given by Gandhi *et al.*[6]. The values of intrinsic viscosity, K_H reported in ref. 6 and ϕ_m calculated using equation (20) are given in *Table 6*. It is seen that lower ϕ_m values correspond with higher values of K_H. This seems to support the view that lower ϕ_m values are indicative of lower quality of solvent and polymer aggregration.

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