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NOTES

A New One-Point Intrinsic Viscosity Method

INTRODUCTION

The intrinsic viscosity $[\eta]$ of a polymer solution is generally determined by measuring relative viscosities at a series of differing concentrations. In most cases, $[\eta]$ can be evaluated conveniently using the graphic representations of Huggins[1] and Kraemer.[2] This technique and other graphic solutions sometimes fail to provide accurate estimates of $[\eta]$, however, because they imply a linear, two-parameter approximation to an actual power-series relation between relative viscosity and concentration.[3] No two-parameter solution can be generally valid, although each may be useful in a particular context. Nonlinear least-squares fitting of the actual curvilinear relation is a universal method for estimating $[\eta]$ from relative viscosity data at a series of concentrations.[4] This procedure requires machine computations which may not always be as convenient as graphic solutions.

Considerable savings in time and effort would be realized if a determination of relative viscosity at a single concentration could be used to estimate $[\eta]$. A number of workers have proposed such methods.[5–10] Techniques such as that of Solomon and co-workers[5,6] seem; however, to be most reliable for low-concentration data in particular polymer–solvent combinations in which the Huggins' constant[9,11–13] is not far from 1/3. Elliott and co-workers[9,10] have noted that the Martin equation[14] provides useful estimates of $[\eta]$ from single-point measurements when a single slope constant can be assumed for the particular polymer–solvent system. A universal slope constant for all polymer–solvent combinations is not possible in this case.

Many of the single-point methods appear to be useful for given polymer and solvent combinations. None has been demonstrated to be generally reliable without prior validation for unknown systems. This article describes a single-point $[\eta]$ technique which appears to overcome this restriction. It will not be any more useful than any of its predecessors in cases where each of the former can be applied. It does appear to be valid, however, for a wide variety of polymers and solvents without adjustment for the peculiarities of the particular system.

The new method is based on a model for prediction of Newtonian viscosities of concentrated polymer solutions, given the intrinsic viscosity in the particular solvent.[15,16] An initial, semiempirical model[15] has been shown to account for viscosities of mixtures of several polymers in a common solvent[17] and for concentration effects in good solvents in gel permeation chromatography.[18] It has also been applied to universal calibration in gel permeation chromatography[19] and to the characterization of false viscosity in cellulose acetate solutions.[20]

A more recent modification of the theory[16] is less empirical and somewhat easier to apply. Both models give essentially equivalent viscosity predictions in fairly dilute polymer solutions.

The second model can be used to estimate viscosities of concentrated solutions from a measured value of relative viscosity at a single concentration.[21] The technique described here is analogous to the latter calculations. The model presented assumes the existence of noninterpenetrating solvated spherical polymer entities. This assumption must fail at sufficiently high concentrations, and this limits application of the single-point method for estimation of concentrated solution viscosities[16,21] This problem is not a factor in calculation of $[\eta]$ because the concentrations used must be chosen to avoid intermolecular interference.

THEORY

The reader is referred to the original article[16] for complete derivation of the basic model, which employs a relation between relative viscosity and volume fraction of solvated polymer along with a calculation of the effects of concentration on hydrodynamic volume of solvated polymer molecules. The equations needed for the present calculation of $[\eta]$ follow.

TABLE I
Comparison of Single- and Multipoint Intrinsic Viscosities

				Experimental		Calculated	
Polymer	Molecular weight	Solvent	Temp., °C	Ref.	$[\eta]$, dl/g	$[\eta]$, dl/g	Single-point concentration, g/dl
Polystyrene	$\overline{M}_w$ 1.46 × 10^6	Toluene	30	24	2.60	2.59	0.515
	$\overline{M}_w$ 1.08 × 10^6		30	24	1.93	1.90	0.600
	$\overline{M}_w$ 0.5 × 10^6		30	24	1.15	1.14	0.525
Polystyrene	$\overline{M}_w$ 1.46 × 10^6	6:1 (vol) 2-butanone:isopropanol	23	24	0.89	0.93	0.365
	$\overline{M}_w$ 1.46 × 10^6				0.89	0.91	0.28
	$\overline{M}_w$ 1.08 × 10^6				0.79	0.86	0.534
	$\overline{M}_w$ 1.08 × 10^6				0.79	0.82	0.28
	$\overline{M}_w$ 0.5 × 10^6				0.52	0.52	0.515
Polystyrene	$\overline{M}_w$ 370,000	Benzene	25	25, 26	1.35	1.32	4.0
						1.30	2.0
						1.32	1.0
						1.34	0.5
						1.35	0.25
Polystyrene	M ~ 250,000	2-butanone	25.0	27	0.63	0.63	1.0
						0.62	0.5
		Benzene	25.0	27	1.10	1.13	1.0
		Toluene	25.0	27	1.02	1.06	1.0
						1.05	0.5
						1.04	0.25

Poly(ethyl-methacrylate)		6:1 ethyl acetate:ethanol	35.0	6, 28	1.246	1.23	0.3
						1.20	0.05
					4.200	4.34	0.3
						4.27	0.05
					9.700	9.11	0.3
						9.65	0.05
Poly(methyl methacrylate)	71,000	Toluene	25.06	29	2.48	2.66	2.55
						2.61	1.95
	280,000	Toluene	25.06	29	6.76	6.38	0.96
						6.49	0.78
Polyethylene		Decalin	135	9	26.9	32.8	0.1
						28.9	0.037
					19.7	19.9	0.1
					2.32	2.55	0.3
						2.47	0.14
					2.19	2.36	0.2
Polypropylene		Decalin	135	9	1.43	1.47	0.5
					8.54	9.31	0.2
					2.32	2.37	0.5
Hydroxyethyl cellulose		Water	25.0	10	17.0	19.5	0.05
					14.2	15.9	0.05
					9.3	10.0	0.05
					3.7	3.8	0.1

The volume fraction ϕ of swollen polymer molecules in solution at concentration c (g cm^{-3}) is given by

$$\phi = \frac{0.524c\epsilon_0}{0.524\rho + c(\epsilon_0 - 1)} \tag{1}$$

where ρ is the density (g cm^{-3}) of the amorphous polymer at the solution temperature, and the infinite dilution swelling factor ϵ_0 is obtained from

$$\epsilon_0 = \frac{\rho[\eta]}{2.5} \tag{2}$$

The use of eq. (1) is confined in theory to concentrations such that $0 \leq c \leq 0.524\rho$, because of the assumption in the model of a high concentration boundary condition corresponding to cubic packing of uniform spheres.

With ϕ from eq. (1), the Newtonian flow of suspensions of polymeric spheres is described by[16,22]

$$\frac{\eta_0}{\eta} = 1 - 2.5\phi + 11\phi^5 - 11.5\phi^7 \tag{3}$$

where η_0 and η are the solvent and solution viscosities, respectively. If the (η_0/η) ratio is known at a single concentration, eq. (3) may be solved for ϕ. The resulting value and the known c yield a value of ϵ_0 in eq. (1), and this gives $[\eta]$ from eq. (2). Equations (1) and (2) can be combined to give

$$[\eta] = \frac{\phi(1.31\rho - 2.5c)}{(c\rho)(0.524 - \phi)} \tag{4}$$

Equations (3) and (4) then yield $[\eta]$, with given (η_0/η) and the corresponding c.

RESULTS

The roots of eq. (3) with given (η_0/η) were calculated with a successive quadratic factorization algorithm[23] (IBM subroutine PRBM, DPRBM). Only one of the seven roots obtained is real, positive, and within the range $0 \leq \phi \leq 0.524$, as required by the model. There is thus no ambiguity in the selection of the ϕ value for use with the corresponding c term to estimate $[\eta]$ from eq. (4).

Table I compares $[\eta]$ values obtained by this method with corresponding multipoint values. The comparisons were selected from the literature for difficult systems in which polymer molecular weight is high and some solvents are not thermodynamically good. The conventional multipoint plots tend to be curved in these cases and uncertainties in single-point model assumptions are usually emphasized. Solutions which approach more ideal behavior of Huggins and Kraemer plots are omitted for the sake of brevity, since the present model and other single-point methods will work well in these cases.

The second entry in Table I is of particular interest since the butanone/isopropanol mixture is a theta solvent for polystyrene.[24] Although the basic model accounts for the inverse dependence of hydrodynamic volume on concentration in good solvents,[18] it is not effective in theta systems where the extent of solvation is essentially independent of concentration.[30] The estimated $[\eta]$ values are nevertheless fairly close to multipoint figures although the calculated $[\eta]$ may depend slightly on the particular reference concentration, as shown in Table I for higher molecular weight polymers.

The model may also be used, of course, to calculate the entire relative viscosity (η/η_0)–c relation. This involves use of the calculated ϵ_0 in reverse sequence, eq. (1)–eq. (3), to estimate η_0/η at different concentrations. The resulting values can be used to construct Huggins[1] and Kraemer[2] plots for linear extrapolation to zero c and consequent estimation of $[\eta]$. Table II shows the results of such calculations for the first two entries in Table I, comprising polystyrenes in a good solvent (toluene) and the particular theta solvent.

TABLE II
Solution Properties of Polystyrenes

			Experimental[24]				Calculated		
Polymer $\bar{M}_w$	Solvent	Temp., °C	Concn., g cm^{-3} $\times 10^2$	η/η_0	$[\eta]$, cm^3 g-l.	K_1[b]	η/η_0	$[\eta]$, cm^{-3} g-l.	K_1
1.46×10^6	toluene	30	0.515[a]	2.91	260	0.32	2.91	259	0.32
			0.375	2.28			2.27		
			0.320	2.03			2.05		
			0.245	1.77			1.76		
			0.200	1.60			1.60		
			0.150	1.44			1.44		
			0.090	1.25			1.25		
1.08×10^6	toluene	30	0.600[a]	2.57	193	0.29	2.57	190	0.33
			0.490	2.21			2.22		
			0.350	1.83			1.81		
			0.325	1.73			1.74		
			0.250	1.56			1.55		
0.5×10^6	toluene	30	0.525[a]	1.71	115	0.29	1.71	114	0.30
			0.465	1.60			1.62		
			0.315	1.40			1.40		
			0.240	1.29			1.30		
			0.125	1.15			1.15		
1.46×10^6	6:1 (vol) 2-butanone: isopropanol	23	0.365[a]	1.37	89.0	0.89	1.37	92.7	0.11
			0.280	1.27			1.28		
			0.225	1.22			1.22		
			0.170	1.15			1.17		
1.46×10^6			0.365	1.37	89.0	0.89	1.36	91.0	0.22
			0.280[a]	1.27			1.27		
			0.225	1.22			1.22		
			0.170	1.15			1.16		
1.08×10^6		23	0.540[a]	1.53	79.0	0.72	1.53	86.0	0.28
			0.280	1.24			1.26		
			0.180	1.15			1.16		
			0.100	1.08			1.09		
1.08×10^6		23	0.540	1.53	79.0	0.72	1.49	81.6	0.38
			0.280[a]	1.24			1.24		
			0.180	1.15			1.15		
			0.100	1.08			1.08		
0.50×10^6		23	0.515[a]	1.29	52	0.27	1.29	52	0.27
			0.375	1.21			1.21		
			0.290	1.16			1.16		
			0.240	1.13			1.13		

[a] Experimental (η/η_0) at this concentration used in eq. (3) as calibration value for the model described in text.

[b] Huggins constants were calculated from eq. (5) from linear least-squares fits to the data listed in this table.

It is not surprising that the calculated relative viscosities are very close to the experimental values in toluene solutions,[16,21] but the theta solvent figures are also surprisingly good estimates.

The procedure described also affords an estimate of Huggins' constant K_1 from the equation[1]:

$$\frac{1}{c}\left(\frac{\eta}{\eta_0} - 1\right) = [\eta] + K_1[\eta]^2c \tag{5}$$

Although the relative viscosities listed in Table II are close to experimental values, the calculation of Huggins' constant, for which results are also listed, is not as satisfactory. These slope constants were calculated from the experimental and estimated data using (η/η_0) figures rounded to two decimal places, to correspond to the original reference.[24] The resulting Huggins' constants are very sensitive to rounding-off variations since K_1 is the quotient of the slope of the$[(\eta - \eta_0)/c\eta_0]$–$c$ plot divided by the square of the intercept. Thus, although the model predicts the slopes and intercepts very well, it does not seem to be reliable for estimation of K_1.

It may be questioned, indeed, whether the Huggins constant is sufficiently free of inadvertent experimental uncertainty to be an unequivocal property of the polymer–solvent system. Equation (5) is a truncated version of a virial equation in concentration,[31] and K_1 or any other linear slope parameter reflects the approximation of a chord to a real curve. The value measured may depend on the particular experimental concentrations to an extent which can be significant compared to the limited range of K_1.

We are obliged to conclude, then, that calculation of Huggins constants from single-point viscosity data is not likely to be a fruitful exercise.

Returning to Table I, it can be seen that the model used predicts polystyrene $[\eta]$ values accurately in many solvents, and that choice of a particular concentration for calculation has little effect in the range normally used for multipoint $[\eta]$ measurements.

The data for poly(ethyl methacrylate) are for high molecular weight polymers which have been shown to be amenable to the Solomon's single-point $[\eta]$ calculations.[6] This again is a theta system[28] which presents an extreme test for the present model, particularly with high molecular weight polymers. The coincidence shown seems to be good.

The poly(methyl methacrylate)–toluene data given in Table I are for a system in which the Huggins and Kraemer plots are not as satisfactory as usual.[29] The present model estimates $[\eta]$ values which coincide with multiconcentration estimates to within a few per cent.

The polyethylene and polypropylene data are also examples of cases in which eq. (5) does not represent experimental values very well.[9] The single-point method of Solomon and Ciuta[5] is reported not to be effective here for concentrations such that $[\eta]c > 1$. Elliott and co-workers[9] have found that a useful single-point $[\eta]$ estimate can be obtained by assuming a universal slope constant in the Martin equation.[14] This constant will not apply to other polymer–solvent systems. The present model is shown in Table II to predict experimental $[\eta]$ figures to an accuracy which should be satisfactory for most practical purposes. The raw data for polyethylene were read from the published Huggins plots, while the polypropylene relative viscosities were reconstructed from the reported Martin equation correlations.[9] Use of actual measured values might be expected to improve the reliability of the calculated $[\eta]$ figures.

In the hydroxyethyl cellulose–water system listed in Table I, a single-point $[\eta]$ method is also applicable using the Martin equation with a different slope constant from that in polyolefin–decalin solutions mentioned above.[10] The present model also provides useful $[\eta]$ estimates, even with very high molecular weight polymers. This polymer–solvent combination was of interest because application of the basic model seems to be restricted to relatively low concentrations in hydrogen-bonding systems.[16]

CONCLUSIONS

The systems in Table I are chosen deliberately to emphasize possibilities for discrepancies between multipoint and single-point $[\eta]$ values. The new model appears to be generally useful and reliable although there will be extreme cases in which the calculated intrinsic viscosity will depend to some extent on the particular relative viscosity which is chosen as a reference. It seems clear that the method will provide accurate $[\eta]$ estimates in most cases of practical interest.

It is possible to use intrinsic viscosities in a series of solvents to measure $\bar{M}_w$, if Mark-Houwink relations are known for the polymer in each solvent.[32] Conventional multipoint measurements of $[\eta]$ in the three or four solvents required for this method are at least as time consuming as a light-scattering determination of $\bar{M}_w$. Use of the single-point method described here will reduce the experimental effort considerably and make the intrinsic viscosity estimate of $\bar{M}_w$ more efficient.

Production of polymers like PVC and some synthetic fiber formers is routinely controlled on relative viscosities at various concentrations. Calculation of $[\eta]$ values from a reliable single-point method would result in a useful consolidation of data from different suppliers. The model proposed seems to be generally applicable for this purpose.

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