NOTES

Calculation of Concentrated Solution Viscosities from Single-Point Measurements

INTRODUCTION

Previous articles from this laboratory have described a method for prediction of Newtonian viscosities of concentrated polymer solutions, given the polymer intrinsic viscosity in the particular solvent.[1,2] The model used employs a relation between volume fraction of solvated polymer and relative viscosity which was initially proposed for suspensions of solid spheres.[3] Expressions for suspensions cannot be translated directly to polymer solutions because the hydrodynamic volume of solvated polymers is a decreasing function of concentration[4-6] as well as a direct function of polymer molecular weight and polymer–solvent interactions. The problem thus resolves into provision of a method for predicting the dependence of effective hydrodynamic volume on concentration (c), molecular weight (M), and goodness of solvent. Once this question has been resolved, volume fraction of solvated polymeric spheres can be calculated, assuming that the equivalent hydrodynamic sphere is impenetrable to solvent. The resulting viscosity increase can then be estimated from an appropriate expression for suspensions.

The effective hydrodynamic volume of a solvated polymer molecule reflects the influences of solute concentration and molecular size and the extent of solvation. Concentration is given in the statement of the problem. The remaining parameters, molecular weight and polymer–solvent affinity, are characterized together in terms of the intrinsic viscosity of the macromolecular sample in the particular solvent. The viscosity of solutions at given concentrations can be predicted with knowledge of the intrinsic viscosity and an estimate of the density of the amorphous polymer at the solution temperature.[2]

An initial semiempirical model[1] has been shown to account for viscosities of mixtures of several polymers in a common solvent[7] and for concentration effects in gel permeation chromatography.[8] It has also been applied successfully to universal calibration in gel permeation chromatography.[9] Johnston and Sourirajan[10] have used this model to characterize the false viscosity of cellulose acetate solutions. Solution viscosities of a particular sample of this polymer depend on the source of the parent cellulose,[11] and the theory presented cannot predict these viscosities, except at dilute concentrations.[12,13]

A more recent modification[2] of the theory is less empirical and gives somewhat better predictions at higher concentrations. Both models give essentially equivalent viscosity predictions in fairly dilute polymer solutions.

The newer model[2] is simple and easy to apply. To preserve the predictive character of the theory, it has been necessary to make some simplifying assumptions which are discussed in the original article[2] and which cannot accord with all the properties of real polymers. The concepts used in this model are justified only by the predictive ability, simplicity, and usefulness of the final theory. The model presented assumes the existence of noninterpenetrating solvated spherical polymeric entities. This assumption cannot hold at sufficiently high concentrations, where entanglement effects will be noticed and the viscosities predicted on the basis of the present theory must be expected to be lower than experimental values.

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The limiting concentration at which the model is effective is inversely proportional to polymer molecular weight, as expected from the above considerations. Thus, the viscosity of a cyclohexanone solution of 26,000 molecular weight poly(vinyl chloride) (PVC) is predicted at a concentration of 16% (w/v) from the intrinsic viscosity of the polymer. The corresponding limiting concentration for reliable predictions is, however, only around 2% for PVC molecular weights[2] of 150,000. Similar effects are noted for aqueous solutions of poly(vinyl alcohol) and polyacrylamide, but the latter limiting concentrations are lower than for PVC–cyclohexanone, as would be expected from the hydrogen-bonding interactions between the former solutes and water. The present report describes a method for extending the predictions of solution viscosity into higher concentration regions.

The theory[2] used initially is based on an experimental viscosity at zero concentration, i.e., the intrinsic viscosity at infinite polymer dilution. We show here that solution viscosities can be derived from a single-concentration experimental viscosity which need not be the intrinsic viscosity. This has advantages beyond the primary aim of extending the predictive character of the model to concentrations higher than those at which viscosities can be reliably estimated using the limiting viscosity number as a benchmark. Practical formulations can often not be characterized in terms of an intrinsic viscosity. The solvent may be a mixture of components, and the "solute" may be considered to be a mixture of resins or polymers and pigments. The present extension of the original model appears to be applicable to such systems given an experimental value of viscosity at a particular polymer concentration. The theory may be particularly useful for estimation of changes in solution viscosities which result when polymer concentration is changed by thinning a practical formulation or when compatible polymer solutions are blended.

THEORY

The present model is a direct extension of the initial theory which was based on predictions from known values of intrinsic viscosity. The reader is referred to the original reference[2] for a complete derivation of the basic model.

The volume fraction ϕ of swollen polymer molecules in solution at concentration c (g/cm³) is given by

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

where ρ is the density (g/cm³) of the amorphous polymer at the solution temperature, and the infinite dilution swelling factor ϵ_0 is obtained from the intrinsic viscosity $[\eta]$ by

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

The use of eq. (1) to calculate ϕ is confined in theory to concentrations such that $0 \leq c \leq 0.524\rho$, because of the assumption in the initial model of a high concentration boundary condition corresponding to cubic packing of uniform spheres. We emphasize that the basic model does not generally predict viscosities up to a concentration equal to 0.524ρ. This concentration is used as a convenient benchmark which can be justified on geometric grounds. It helps preserve the predictive capacity of the model. We do not imply that the equivalent hydrodynamic spheres will not actually interpenetrate at lower concentrations. (When they do, of course, the predicted viscosities tend to be too low.)

With ϕ from eq. (1), the Newtonian flow of suspensions of polymer spheres (assumed shape) is described by

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

where η_0 and η are the solvent and solution viscosities, respectively.

In the form given, the estimation of η at concentration c requires a prior knowledge of $[\eta]$, in order to calculate ϵ_0 for use in eq. (1). In some cases, $[\eta]$ may not be available, as with mixed solvents or polymer samples with variable and unspecified branching or copolymer composition. This communication shows that the basic model may still be used if the (η_0/η) ratio is known at one concentration. Equation (3) is solved for ϕ under the given experimental conditions. The resulting value of ϕ and the corresponding c value in eq. (1) yields an ϵ_0 figure which can be applied in reverse sequence [eq. (1)–eq. (3)] to estimate ϕ and hence η at different concentrations.

The procedure outlined here is a straightforward application of the initial model. Calculation of ϵ_0 from a finite concentration viscosity through eqs. (3) and (1) may take into account the intermolecular effects which have occurred between solute molecules up to the calibration concentration. It should thus be expected that the use of an effective ϵ_0 will facilitate prediction of solution viscosities at concentrations higher than those attained by use of a "real" ϵ_0 [from eq. (2)]. The model is still based on the behavior of noninteracting spherical hydrodynamic spheres. If intermolecular effects become even more significant at concentrations higher than the calibration level, the new model will also fail to predict the resulting higher viscosities. It can thus be expected that the procedure given in this article will be more effective for prediction of effects of dilution from a calibration solution than for results of further concentration.

RESULTS

The roots of eq. (3) with given (η_0/η) were calculated by means of a successive quadratic factorization algorithm[14] (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 figure to estimate ϵ_0 from eq. (1). This ϵ_0 is then used in subsequent calculations at different c values to estimate ϕ and solution viscosities.

As mentioned, viscosity predictions based on intrinsic viscosity as a benchmark tend to be lower than actual values at concentrations where intermolecular interactions may become significant,[2] since the model assumes that the solute molecules act as independent agents. Where this may be a problem, the modified approach used here can be an advantage. We illustrate the difference between viscosity predictions based on intrinsic viscosity and on a finite concentration viscosity with some data of Weissberg and co-workers[15] on polystyrene solutions, as summarized in Table I.

The present model shows only a slight advantage over the initial, intrinsic viscosity-based theory, for solutions of a 58,000 molecular polystyrene in toluene (Table Ia). This is because the initial model yielded predictions which were consistent with experiment up to the highest concentration (6%) used. Calibration of the model with the viscosity of a 3.28% solution instead of that of an infinitely dilute mixture, as shown, results in little change.

The advantages of the revised procedure are more apparent in the data in Table Ib for a 146,000 molecular weight polystyrene in the same solvent. The relative viscosities predicted from the $[\eta]$ reference mark deviated from experimental figures at concentrations ≥ 4 g/dl. When the measured viscosity at 4.66 g/dl was taken as the benchmark, as shown, the reliability of the predictions could be extended usefully up to about 7.5 g/dl concentration. It is particularly striking that the use of the higher concentration reference value did not cause any significant deterioration in viscosity predictions at lower concentrations.

Similar results are shown for toluene solutions of a 600,000 molecular weight polymer in Table Ic. The better predictability at higher concentrations without serious disadvantages at lower concentrations is illustrated by this comparison in which estimates were made from concentrations of zero (i.e., $[\eta]$), 0.78, and 1.85 g/dl of this high molecular weight polymer. In this example, use of the highest of the three concentrations as a reference value seems to confer advantages at higher predicted viscosities and relatively few disadvantages in solutions more dilute than the standard.

TABLE I
Comparison of Viscosity Predictions

Concentration, g/dl	Relative Viscosity		
	Experimental[15]	Predicted from $[\eta]$	Predicted from η

(a) 58,000 Molecular Weight Polystyrene in Toluene (30°C)

Concentration, g/dl	Experimental[15]	Predicted from $[\eta]$	Predicted from η
0.117	1.04	1.04	1.04
1.170	1.49	1.49	1.49
2.320	2.12	2.11	2.10
3.984	3.28	3.31	3.28 (std.)
5.154	4.29	4.39	4.34
5.927	5.07	5.23	5.17

(b) 146,000 Molecular Weight Polystyrene in Toluene (30°C)

Concentration, g/dl	Experimental[15]	Predicted from $[\eta]$	Predicted from η
0.043	1.03	1.03	1.03
0.101	1.07	1.07	1.07
0.880	1.76	1.74	1.75
1.724	2.68	2.70	2.74
2.615	4.13	4.02	4.11
3.526	5.92	5.75	5.89
4.664	8.72	8.48	8.72 (std.)
6.219	14.26	13.39	13.82
7.462	20.14	18.44	19.06
8.111	24.06	21.52	22.27
9.328	32.47	28.22	29.24

(c) 600,000 Molecular Weight Polystyrene in Toluene (30°C)

Relative viscosity

Concentration, g/dl	Experimental[15]	from $[\eta]^2$	Predicted from η	from η
0.018	1.04	1.04	1.04	1.04
0.362	1.95	1.89	1.99	1.94
0.637	2.92	2.79	3.01	2.90
0.777	3.49	3.34	3.63	3.49 (std.)
1.267	6.14	5.70	6.35	6.03
1.655	9.07	8.09	9.13	8.62
1.851	10.75	9.48	10.75 (std.)	10.12
2.069	13.03	11.17	12.72	11.96
2.263	15.21	12.80	14.63	13.73
2.545	19.01	15.42	17.70	16.57
2.909	24.75	19.20	22.13	20.68

(d) 80,800 Molecular Weight Poly(4-vinylbiphenyl) in Benzene (30°C)

Relative viscosity

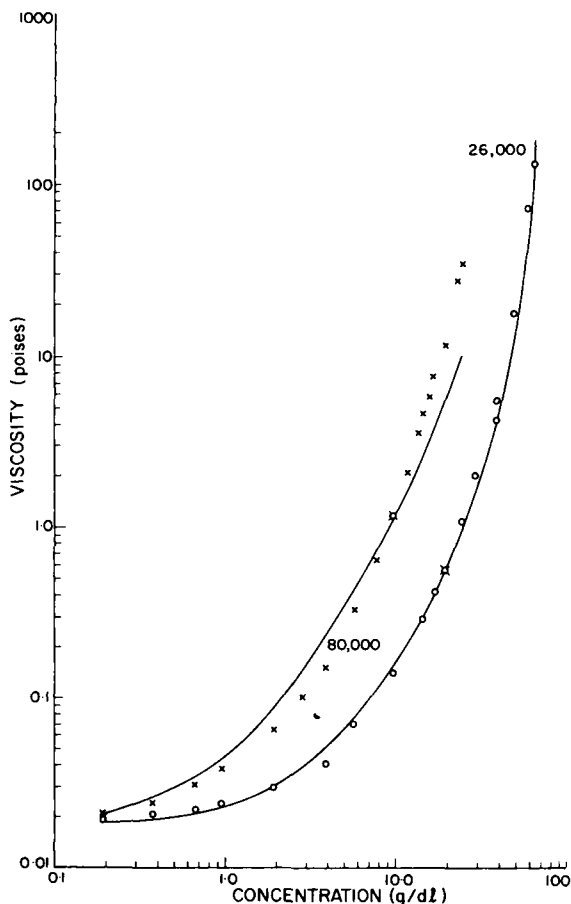| Concentration, g/dl	Experimental[16]	from $[\eta]$	Predicted from η	from η
0.869	1.22	1.22	1.22	1.24
2.192	1.61	1.61	1.62	1.69
3.064	1.92	1.92	1.93	2.04
4.620	2.59	2.56	2.59	2.79
6.723	3.70	3.70	3.75	4.13
8.206	4.75	4.72	4.79	5.33
10.405	6.73	6.62	6.73 (std.)	7.59
13.391	10.56	10.15	10.33	11.82
16.085	15.94	14.57	14.86	17.15
19.089	24.34	21.42	21.89	25.33
20.925	21.12	26.93	27.51	32.10 (std.)

Fig. 1. Viscosity and concentration of cyclohexanone solutions of poly(vinyl chloride); date of ref. 17. Polymer molecular weights are as shown. Lines are predicted from calibration values marked ӿ. Symbols are experimental points.

Table Id contains data from a poly(4-vinylbiphenyl) solution in benzene[16] which extend up to higher relative viscosities than the values cited above for polystyrene. Predictions with the model using $[\eta]$ as standard coincide with experimental values to within 4% of the latter value up to concentrations near 13% (w/v). Use of the experimental 10% concentration viscosity as a calibration value permits an estimation of the viscosity of 20% solutions which is about 10% too low. This standard yields viscosities of more dilute solutions with an almost negligible error. When the 21% solution is used as standard, the relative viscosities calculated for more dilute mixtures deviate from experimental values by 1% or 2% of the measured figures. This accuracy is probably adequate for many practical purposes.

The last example shows that the viscosity–concentration curve estimated from a concentrated solution experimental value tends to coincide at the reference value and in very dilute concentrations. The shape of the curve at intermediate concentrations may deviate from the experimental relation at intermediate concentrations if the concentration range is large. Whether or not this deviation is serious depends on the particular application for which the calculations are intended.

This point is illustrated further with poly(vinyl chloride)–cyclohexanone data of Pezzin and Gligo.[17] Plots of experimental and predicted viscosities for polymers with molecular weights of 26,000 and 80,000 are shown in Figure 1. It will be noted that the
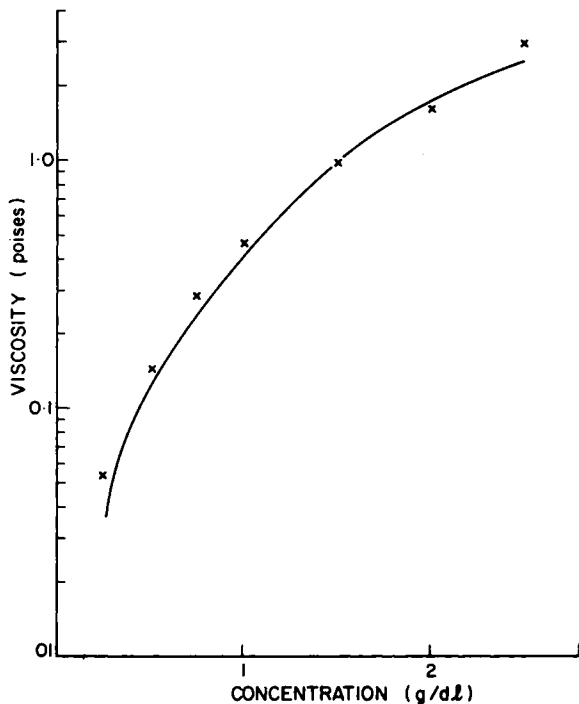
Fig. 2. Viscosity–concentration data for Dow Methocel 90 HG in water at 25°C.[20]   Line is predicted using 2% concentration.

calculated values (which are based on the viscosity of a 19% solution in this case) coincide with experimental values at all concentrations between 0.2% and 61%.   The initial model,[2] based on [η], was useful up to about 19% concentration.   The agreement of estimated and measured viscosities is not as good for an 80,000 molecular weight polymer.   Calibration in this case was against the experimental value at 9.4% concentration. Higher concentration estimates fall below the experimental values as expected from the assumption in the model that intermolecular entanglement effects are absent.   Estimated viscosities for the 80,000 molecular weight polymer at concentrations below the reference value tend to be somewhat higher than experimental points in Figure 1.

It is appropriate at this point to emphasize that the theory presented here predicts Newtonian viscosities only.   Some of the values reported for the more viscous solutions of Pezzin and Gligo[17] are not experimental Newtonian viscosities, but are estimates obtained by extrapolation from non-Newtonian flow regions.   Potential errors in such extrapolations have been pointed out elsewhere.[18,19]   There is a danger in this connection that the extrapolated Newtonian viscosity may be higher than the corresponding actual value.   The errors, if any, in such extrapolations vary between polymer systems and cannot be estimated a priori.   If the higher viscosity values cited suffered from such uncertainties, the model predictions would indeed deviate as shown for the 80,000 molecular weight sample, when they are based on an extrapolated Newtonian viscosity value.

The data of Gillespie[20] for dilute aqueous solutions of methyl cellulose are a case in point, as these systems were non-Newtonian at concentrations greater than about 0.5% and Newtonian viscosities were estimated by extrapolation.   As shown in Figure 2, the theory nevertheless anticipates viscosities in the range between 0.03 and 3.0 poises to within about 10% of the reported values, using a calibration input at 2% concen-
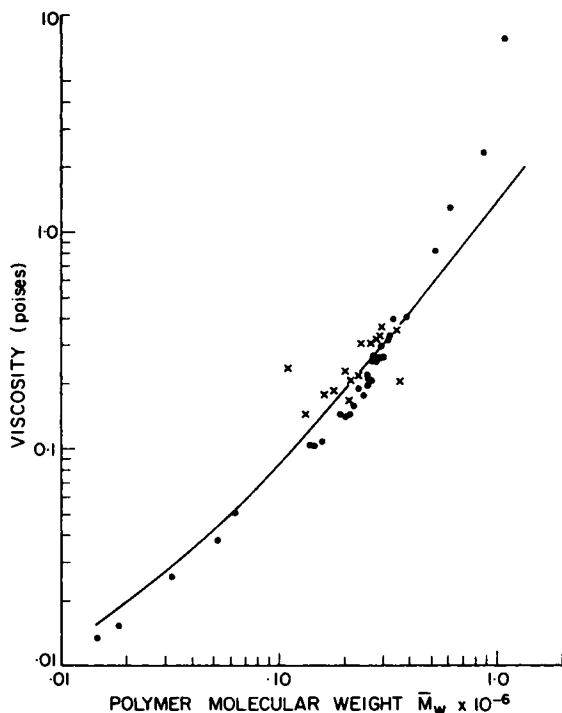
Fig. 3. Plot of 25°C viscosities of 10% (w/v) solutions of polystyrenes in toluene: (●) data of Keskkula and Taylor[22]; (×) data of Rogers[21]; line—viscosity predicted from intrinsic viscosity with theory described in ref. 2.

tration. The concentration range here includes most methyl cellulose solutions of practical interest.

Along similar lines, Rogers[21] has pointed out that structural effects in concentrated polystyrene solutions may influence viscosity measurements. Viscosities of 10% solutions in toluene are used for production control in manufacture of this polymer. Figure 3 shows reported viscosity–molecular weight ($\bar{M}_w$) data for polystyrene, as reported by Rogers[21] and by Keskkula and Taylor.[22] There is evidently considerable scatter at equivalent molecular weight. These discrepancies may reflect experimental uncertainties in measurements of Newtonian viscosities as well as the effects of differences in molecular weight distributions of the various polymers. The same figure shows the viscosity computed with our model based on intrinsic viscosity [eqs. (1) and (3)] with ϵ_0 in this case given by

$$\epsilon_0 = \frac{\rho[\eta]}{2.5} = \frac{KM^\alpha \rho}{2.5}. \qquad (2a)$$

In eq. (2a), K and α are the Mark-Houwink constants[23] reported for polystyrene in toluene. The predictive accuracy is very good in this case, considering that the theory has no adjustable parameters and the calculations are based on $\bar{M}_w$ alone.

DISCUSSION

The model suggested here and in the preceding article on this topic[2] provides a rapid, convenient estimation of solution viscosity from a measured viscosity at a single con-

centration. If no experimental values are available, the appropriate Mark-Houwink relation may be used to calculate a benchmark value at zero concentration. Use of a reference viscosity at a particular concentration extends the reliability of estimated viscosities to higher concntrations than are generally attainable through use of $[\eta]$.

The predictive nature of the theory prevents inclusion of any adjustable parameters. All polymer molecules are assumed to be noninterpenetrating if the intrinsic viscosity is used as a reference point or to have a constant degree of interaction if a finite concentration viscosity is employed instead. This implies no allowance for effects of molecular weight distribution. The latter restriction is significant only if the reference viscosity value is to be used to estimate the results of changing polymer molecular weight, since only a single average molecular weight can be employed in this calculation. The average value of choice is $\bar{M}_v$ in the particular solvent, but this figure is not always available, as in the examples given.

The theory has been deliberately kept simple to make it easy to use and to permit predictions without recourse to experiment. The accuracy of the estimated values appears to be good for most practical purposes, provided the extrapolation is not extended to concentrations in which serious entanglement effects will occur. The parameters used are justified by the predictive ability of the model. Theories which are more comprehensive or perhaps more satisfying intellectually are generally not useful for the purposes for which the present model is intended.

Methods of data treatment based on reduced variable techniques may be effective in consolidating viscosity results over wider concentration ranges than the present model. Prime examples are the methods of Simha and co-workers[16] and models based on the Martin equation.[24,25] These techniques differ from the present model in requiring two experimental data points rather than the single-concentration value used in the present theory except when a general value of one of the specified parameters may be assumed for a particular polymer–solvent system.[26]

The theory used in this and the preceding article[2] is based on a particular viscosity-concentration relation for suspensions and a specific packing geometry to calculate change of polymer volume fraction with concentration. It seems quite possible that combinations of other assumptions in these two respects would yield viscosity estimates similar to those obtained with this theory if used with the other basic concepts in the model.

The theory presented can evidently be used to estimate zero concentration viscosity, and hence $[\eta]$, from a single-point measurement. This application will be reported separately.

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