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Shear-Thinning of 'Random Coil' Polysaccharides: Characterisation by Two Parameters from a Simple Linear Plot

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ABSTRACT

The shear-thinning behaviour of solutions of conformationally disordered ('random coil') polysaccharides, at concentrations above the onset of coil-overlap and entanglement (i.e. above c), can be matched, with reasonable precision, by the equation:*

$$\eta = \eta_0/[1 + (\dot{\gamma}/\dot{\gamma}_{1/2})^{0{\cdot}76}]$$

Thus viscosity (η) at any shear rate ($\dot{\gamma}$) can be characterised by two parameters: the maximum 'zero-shear' viscosity (η_0) and the shear rate ($\dot{\gamma}_{1/2}$) at which viscosity is reduced to $\eta_0/2$. The values of η_0 and $\dot{\gamma}_{1/2}$ can be derived from, respectively, the intercept and slope of a simple linear plot of η versus $\eta\dot{\gamma}_{0{\cdot}76}$. The method can also be applied to other 'random coil' polymers of reasonably high polydispersity, and to the analysis of the frequency (ω) dependence of dynamic viscosity (η^*) from small-deformation oscillatory measurements.

1 INTRODUCTION

Most polysaccharides exist in solution as fluctuating 'random coils'. At low concentrations the individual coils are free to move independently through the solvent, but at higher concentrations they are forced to interpenetrate one another and can then move only by wriggling ('reptating') through the entangled network of neighbouring chains (De Gennes, 1979). At low shear rates, where the disruption of existing entanglements by the imposed flow is balanced by the formation of new entanglements between different partners, viscosity (η) remains constant at a maximum

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value (the 'zero-shear' viscosity, η_0), but at higher shear rates, where the rate of re-entanglement can no longer keep pace with forced disentanglement, the network is depleted and viscosity falls.

For samples with a wide polydispersity of chain length (i.e. virtually all commercial polysaccharides) the form of shear-thinning is entirely general (Morris *et al.*, 1981). Double-logarithmic plots of viscosity versus shear rate ($\dot{\gamma}$) for different samples are identical in shape and differ only in their position relative to the two axes. The value of η_0 gives a convenient index of the position relative to the viscosity axis; positioning along the shear rate axis can be characterised by the shear rate ($\dot{\gamma}_f$) required to reduce the viscosity to a fixed fraction (f) of the maximum value, η_0 (i.e. $\eta = f\eta_0$ when $\dot{\gamma} = \dot{\gamma}_f$). Thus when measured viscosities are expressed as a fraction of η_0 (i.e. as η/η_0) and applied shear rates are similarly scaled to $\dot{\gamma}_f$ (i.e. as $\dot{\gamma}/\dot{\gamma}_f$) then, as illustrated in Fig. 1 (using an arbitrary value of $f = 0{\cdot}1$), individual flow curves for different samples converge to a single 'master curve', irrespective of primary structure, molecular weight, temperature and solvent conditions. The two parameters η_0 and $\dot{\gamma}_f$ therefore characterise completely the differences in viscosity and shear-thinning for different solutions of commercial 'random coil' polysaccharides.

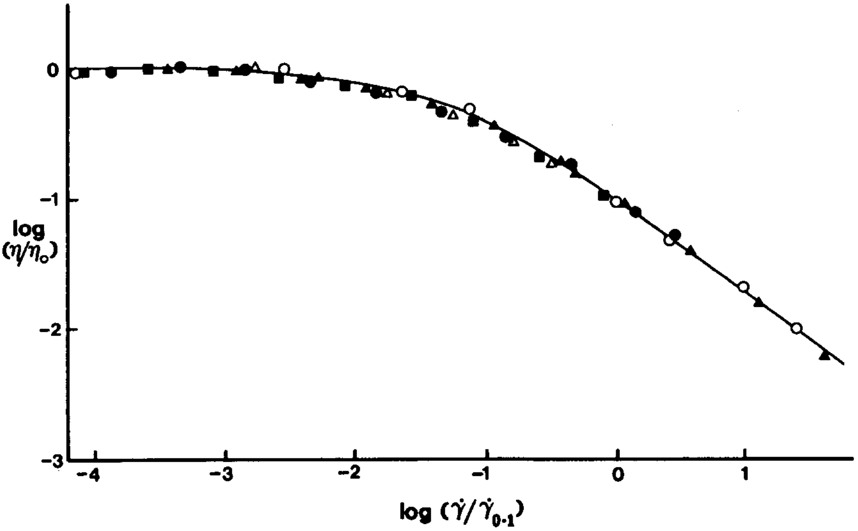

Fig. 1. Generalised shear-thinning curve for 'random coil' polysaccharide solutions (from Morris *et al.*, 1981). Different symbols denote different commercial polysaccharides.

The aim of this paper is to present a simple equation that:

(1) matches, with acceptable precision, the generalised form of shear-thinning illustrated in Fig. 1; and

(2) allows the values of η_0 and $\dot{\gamma}_f$ to be determined from a simple linear plot.

2 THE SHEAR-THINNING EQUATION

A large number of different phenomenological equations have been proposed to match the shear-thinning behaviour of polymer solutions and melts. One of the most successful was developed by Cross (1965) and is of the form:

$$\eta = \eta_\infty + [\eta_0 - \eta_\infty]/[1 + (a\dot{\gamma})^p] \qquad (1)$$

where a and p are adjustable parameters, constant for any specific solution, and η_∞ is the final minimum viscosity attained at very high shear rates (where re-entanglement is abolished). In practice, however, for aqueous solutions of entangled, 'random coil' polysaccharides, the high-shear terminal 'plateau' cannot be accessed, or approached, on any normal viscometer, and η_∞ is negligible in comparison with η_0. Equation (1) can therefore be simplified by setting η_∞ to zero, giving:

$$\eta = \eta_0/[1 + (a\dot{\gamma})^p] \qquad (2)$$

Defining, as above, $\dot{\gamma}_f$ as the shear rate at which $\eta = f\eta_0$, eqn (2) can be recast as:

$$f\eta_0 = \eta_0/[1 + (a\dot{\gamma}_f)^p] \qquad (3)$$

Cancelling η_0 on both sides and rearranging terms then gives:

$$a = [(1 - f)/f]^{-p}/\dot{\gamma}_f \qquad (4)$$

When $f = 0{\cdot}5$, $(1 - f)/f = 1$. Thus $a = 1/\dot{\gamma}_{1/2}$, where $\dot{\gamma}_{1/2}$ is the shear rate required to reduce η to $\eta_0/2$. Equation (2) can therefore be expressed as:

$$\eta = \eta_0/[1 + (\dot{\gamma}/\dot{\gamma}_{1/2})^p] \qquad (5)$$

At low shear rates, where the second term in the denominator is much less than 1, this reduces to $\eta = \eta_0$, corresponding to the low-shear 'Newtonian plateau' region in Fig. 1. At high shear rates, where the first term in the denominator (unity) becomes negligible, the equation becomes:

$$\eta = \eta_0/(\dot{\gamma}/\dot{\gamma}_{1/2})^p \qquad (6)$$

or in logarithmic form:

$$\log \eta = \log(\eta_0 \dot{\gamma}_{1/2}^{p}) - p \log \dot{\gamma} \tag{7}$$

Since, for any specific solution, η_0 and $\dot{\gamma}_{1/2}$ are constant, this is the equation of a straight line of gradient $-p$, corresponding to the high-shear linear region in Fig. 1. Empirically, the final 'terminal slope' of the generalised double-logarithmic shear-thinning plot for commercial 'random coil' polysaccharides has a constant value of $-0{\cdot}76$. Equation (5) can therefore be cast in the final form:

$$\eta = \eta_0 / [1 + (\dot{\gamma}/\dot{\gamma}_{1/2})^{0{\cdot}76}] \tag{8}$$

3 COMPARISON WITH EXPERIMENTAL VALUES

The generalised shear-thinning curve (Fig. 1), derived from an extensive study of many different 'random coil' polysaccharides (Morris *et al.*, 1981), is presented in numerical form in Table 1 and compared with the shear rate dependence generated by eqn (8). In the original investigation, the shear rate reference chosen was $\dot{\gamma}_{0.1}$, the shear rate at which the measured viscosities were reduced to $0{\cdot}1\eta_0$. This does not, of course, affect the form of the curve, but it does necessitate a conversion to the reference value of $\dot{\gamma}_{1/2}$ adopted here. From eqn (8):

$$\eta_0/10 = \eta_0/[1 + (\dot{\gamma}_{0.1}/\dot{\gamma}_{1/2})^{0{\cdot}76}] \tag{9}$$

Hence

$$(\dot{\gamma}_{0{\cdot}1}/\dot{\gamma}_{1/2}) = 9^{(1/0{\cdot}76)} = 18{\cdot}0 \tag{10}$$

Thus

$$\log(\dot{\gamma}/\dot{\gamma}_{0{\cdot}1}) = \log(\dot{\gamma}/\dot{\gamma}_{1/2}) - \log 18{\cdot}0 \tag{11}$$

Using eqn (11) to convert the reported values of $\dot{\gamma}/\dot{\gamma}_{0{\cdot}1}$ to $\dot{\gamma}/\dot{\gamma}_{1/2}$, the ratio of η/η_0 was calculated by eqn (8) for direct, quantitative comparison with the corresponding experimental values.

As shown in Table 1, the overall standard of agreement is excellent; to within about ± 3% at most shear rates. The most serious discrepancies are at low shear rates (in the shear rate range 1–5% of $\dot{\gamma}_{1/2}$), where eqn (8) appears to over estimate the extent of shear-thinning (with a maximum divergence of ~ 6% between observed and calculated viscosities). However, this is the region where the experimental values are least reliable: with decreasing shear rate the measured torque also decreases, with a consequent increase in experimental error. It is also the region

TABLE 1

Comparison of the Generalised Shear-Thinning Curve for 'Random Coil' Polysaccharides with Values Calculated by Eqn (8)

Log$(\dot{\gamma}/\dot{\gamma}_{0\cdot 1})$[a]	$\dot{\gamma}/\dot{\gamma}_{1/2}$[b]	*Log*(η/η_0)			$\eta\,(\%\eta_0)$		
		Observed[a]	*Calculated*[c]	*Difference*	*Observed*[a]	*Calculated*[c]	*Difference*
−4·0	0·0018	0·00	0·00	0·00	100	99	1
−3·5	0·0057	0·00	−0·01	0·01	100	98	2
−3·0	0·0180	0·00	−0·02	0·02	100	96	4
−2·8	0·0286	0·00	−0·03	0·03	100	94	6
−2·6	0·0453	−0·02	−0·04	0·02	95	91	4
−2·4	0·0717	−0·04	−0·06	0·02	91	88	3
−2·2	0·114	−0·07	−0·08	0·01	85	84	1
−2·0	0·180	−0·10	−0·10	0·00	79	79	0
−1·8	0·286	−0·14	−0·14	0·00	72	72	0
−1·6	0·453	−0·18	−0·19	0·01	66	65	1
−1·4	0·717	−0·24	−0·25	0·01	58	56	2
−1·2	1·14	−0·32	−0·32	0·00	48	48	0
−1·0	1·80	−0·40	−0·41	0·01	40	39	1
−0·8	2·86	−0·49	−0·51	0·02	32	31	1
−0·6	4·53	−0·60	−0·62	0·02	25	24	1
−0·4	7·17	−0·72	−0·74	0·02	19	18	1
−0·2	11·4	−0·85	−0·87	0·02	14	14	0
0·0	18·0	−1·00	−1·00	0·00	10	10	0
0·5	57·0	−1·36	−1·35	−0·01	4·37	4·43	−0·06
1·0	180	−1·73	−1·72	−0·01	1·86	1·89	−0·03
1·5	570	−2·11	−2.10	−0·01	0·78	0·80	−0·02
2·0	1800	−2·48	−2·48	0·00	0·33	0·33	0·00

[a] From Table 2 in Morris *et al.*, 1981.
[b] Calculated using eqn (11) to convert $\dot{\gamma}/\dot{\gamma}_{0\cdot 1}$ to $\dot{\gamma}/\dot{\gamma}_{1/2}$.
[c] Calculated from $\dot{\gamma}/\dot{\gamma}_{1/2}$ by eqn (8).

where the percentage error in viscosities taken from the generalised double-logarithmic shear-thinning plot (Fig. 1) is greatest (since the same absolute change in η/η_0 gives a progressively smaller change in $\log(\eta/\eta_0)$ as η approaches η_0). Indeed, when the shear-thinning profile calculated from eqn (8) is also expressed in double-logarithmic form, it is indistinguishable, to well within the experimental error of the original data, from the 'master curve' in Fig. 1.

Thus eqn (8) appears to reproduce very successfully the general form of shear-thinning for commercial 'random coil' polysaccharides.

4 LINEARISATION OF FLOW CURVES

The non-Newtonian flow behaviour ('pseudoplasticity') of polymer solutions is often fitted to a 'power law' of the form:

$$\tau = k\dot{\gamma}^n \tag{12}$$

where τ is the stress generated in resistance to flow, and k and n are constants (n being the so-called 'pseudoplasticity index'). Since, by definition, $\eta = \tau/\dot{\gamma}$, eqn (12) can be recast as:

$$\eta = k\dot{\gamma}^{(n-1)} \tag{13}$$

which in logarithmic form becomes:

$$\log\eta = \log k + (n-1)\log\dot{\gamma} \tag{14}$$

Thus the 'power law' approach is equivalent to treating the generalised shear-thinning curve in Fig. 1 (and the individual flow curves from which it was derived) as a straight line of gradient $(n-1)$ and intercept $\log k$. This is clearly invalid, since in reality the gradient varies from 0 at low shear rates (in the 'Newtonian plateau' region) to $-0{\cdot}76$ at high shear rates (giving values of n anywhere between 1·0 and 0·24). Although, over sufficiently narrow ranges of shear rate, plots of $\log\eta$ versus $\log\dot{\gamma}$ for 'random coil' polysaccharide solutions may appear reasonably linear, the values obtained for k and n are dependent on the shear rates used rather than on the nature of the solution being measured. A valid procedure for plotting 'random coil' flow curves in linear form can, however, be derived by rearranging eqn (8).

Cross-multiplication gives:

$$\eta_0 = \eta + \eta(\dot{\gamma}/\dot{\gamma}_{1/2})^{0{\cdot}76} \tag{15}$$

Hence

$$\eta = \eta_0 - (1/\dot{\gamma}_{1/2})^{0{\cdot}76}\eta\dot{\gamma}^{0{\cdot}76} \tag{16}$$

Thus plotting η against $\eta\dot{\gamma}^{0.76}$ should give a straight line of intercept η_0 and gradient $-(1/\dot{\gamma}_{1/2})^{0.76}$.

Figure 2 shows the generalised shear-thinning curve (Fig. 1) plotted in this way. For simplicity, experimental values of 100 η/η_0 and $\dot{\gamma}/\dot{\gamma}_{0.1}$ (Table 1) have been treated as values of η and $\dot{\gamma}$ respectively. This does not affect the analysis, since the constant 'scaling factors' ($100/\eta_0$ and $1/\dot{\gamma}_{0.1}$) do not alter the form of the graph. The standard of linearity is excellent (again well within the error limits of the original data). The extrapolated value of η_0 is about 3% higher than expected (cutting the vertical axis at 100 $\eta/\eta_0 \cong 103$ rather than 100). As discussed above, however, his small discrepancy may be due, at least in part, to limitations on the accuracy and precision of the viscosity data at low shear rates.

Figure 3 shows shear-thinning data plotted in the same way for a few representative individual solutions of typical commercial 'random coil' polysaccharides. In all cases the standard of linearity is comparable to that shown in Fig. 2 for the generalised 'master curve'.

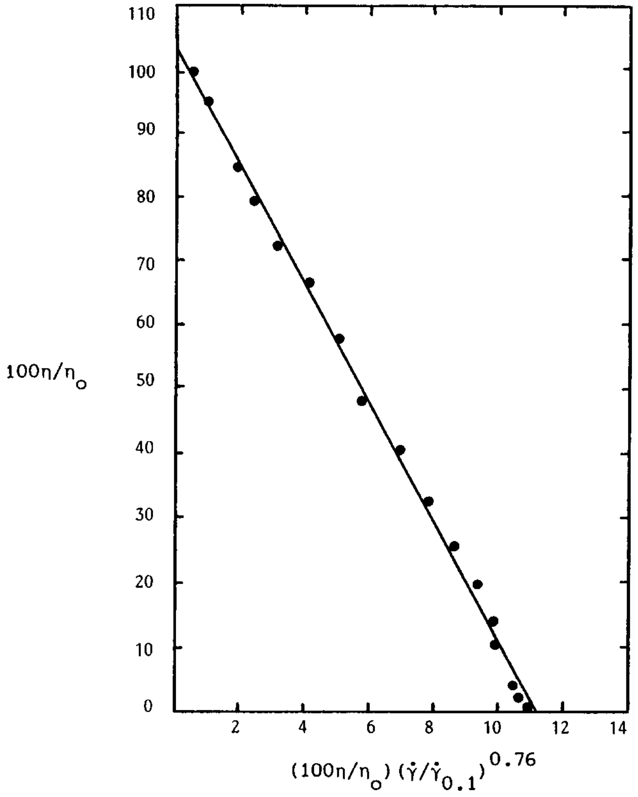

Fig. 2. Generalised shear-thinning of 'random coil' polysaccharides (Table 1) fitted to eqn (16).

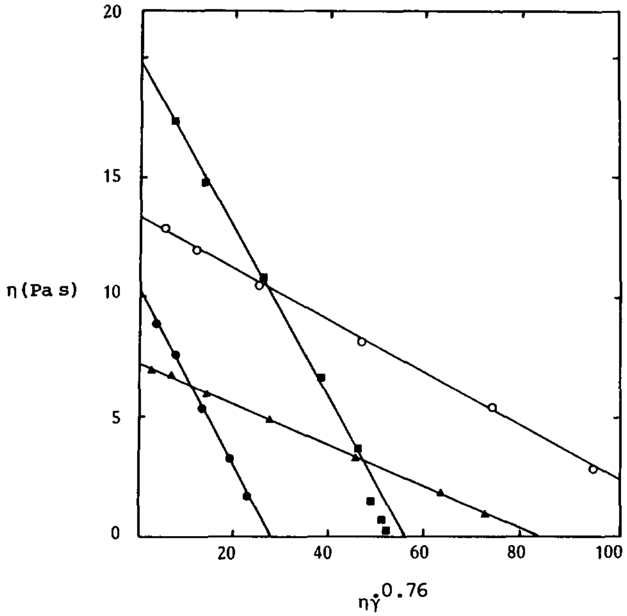

Fig. 3. Shear-thinning plots for locust bean gum (1·34%, ■); alginate (4·5%, ○); pectin (3·16%, ▲) and lambda carrageenan (2·07%, ●). Data taken from Table 1 in Cutler *et al.* (1983).

5 PRACTICAL APPLICATION

The two parameters η_0 and $\dot{\gamma}_{1/2}$ which, in conjunction with eqn (8), completely characterise the flow behaviour of any specific 'random coil' polysaccharide solution, can be determined by the following simple procedure:

(1) Measure the solution viscosity η at a few shear rates (preferably at least 4 or 5) on any available viscometer. Ideally the viscosity should vary by at least a factor of 3 or 4.

(2) At each shear rate ($\dot{\gamma}$) calculate the value of $\dot{\gamma}^{0\cdot76}$ (using the y^x key on a pocket calculator) and multiply the result by the corresponding viscosity value to give $\eta\dot{\gamma}^{0\cdot76}$. If the viscometer used operates at a limited number of fixed shear rates, it may be convenient to keep a note of the corresponding values of $\dot{\gamma}^{0\cdot76}$, which can then be used for future samples.

(3) Plot η (vertical axis) against $\eta\dot{\gamma}^{0\cdot76}$ (horizontal axis) and fit the best straight line (by eye, or using a linear-regression function if available on the calculator used). The intercept on the vertical axis gives η_0.

(4) Calculate the gradient of the straight line (ignoring the negative sign), take the reciprocal, and raise it to the power 1·316 (again using the y^x function). This gives $\dot{\gamma}_{1/2}$.

(5) The viscosity at any other shear rate can then be calculated from η_0 and $\dot{\gamma}_{1/2}$ using eqn (8). The equation can also be used to check the values obtained for η_0 and $\dot{\gamma}_{1/2}$, by comparing calculated and experimental values of viscosity at a few of the experimental shear rates.

A major advantage of this method is that it allows fundamentally valid parameters (η_0 and $\dot{\gamma}_{1/2}$) to be derived without requiring expensive, sophisticated rheological equipment or computer analysis. Indeed measurements on the simplest and cheapest of variable-speed viscometers give values closely similar to those obtained on research quality instruments.

Figure 4 shows the shear-thinning behaviour of a typical 'random coil' polysaccharide solution measured: (a) using cone-and-plate geometry,

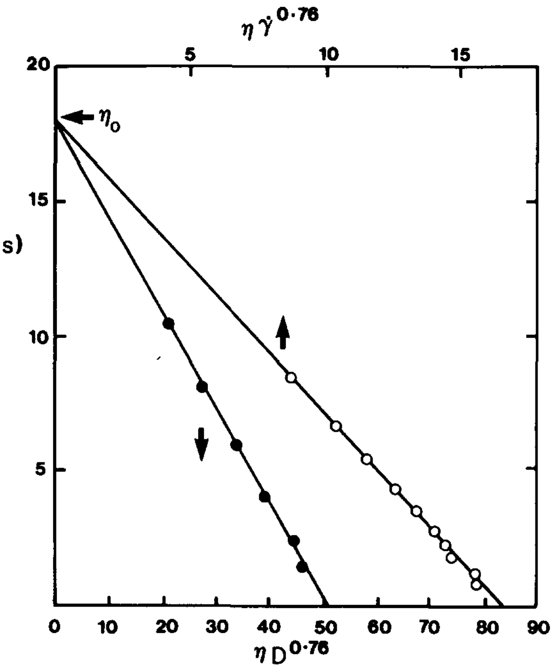

Fig. 4. Linearised shear-thinning plots for a typical solution of guar gum (Meyprogat 150; Meyhall; 1% w/v). Results obtained under an ill-defined shear-regime (●), as a function of spindle-speed (D) on a Brookfield RVT viscometer, extrapolate to a zero-shear viscosity value (η_0) very close to that obtained from measurements at well-defined shear rate ($\dot{\gamma}$) on cone-and-plate geometry (○).

where the shear rate is constant throughout the sample, and (b) under an ill-define shear regime on a Brookfield RVT viscometer, substituting spindle-speed (D) for shear rate in eqn (16). The standard of linearity is comparable for both sets of data, and the extrapolated values of η_0 agree closely.

6 DISCUSSION

Polysaccharide 'thickeners' are normally standardised and marketed on the basis of viscosity measurements at a single, arbitrary shear rate. Since, as shown in Fig. 1, solution viscosity can vary by at least a factor of 100 over the range of shear rates of practical importance, this type of 'single-point' description is, at best, inadequate. More seriously, flow curves for different polysaccharides often cross one another, so that measurements at a single shear rate may even place viscosities at higher or lower shear rates in the wrong order. One purpose of this paper is to show that with very little extra effort, and no additional equipment, the suppliers of commercial polysaccharides could provide a full description of both the maximum viscosity that can be achieved with a particular material (characterised by η_0) and its shear-thinning behaviour (characterised by $\dot{\gamma}_{1/2}$).

Most commercial polysaccharides can be characterised in this way. An obvious exception is starch, where the granule structure gives flow properties different to those of entangled coils. The other major exception is xanthan, which, under most conditions, exists in solution in a rigid, ordered, chain conformation, giving rise to characteristic 'weak gel' properties (Ross-Murphy *et al.*, 1983), including unusual shear-thinning which can be best fitted to a 'power-law' [eqn (14)]. The new commercial bacterial polysaccharides welan and rhamsan, which are also conformationally ordered in solution (Robinson *et al.*, 1988), have similar 'weak gel' properties and again give shear-thinning of the 'power law' type.

A common feature of these systems is that intermolecular interactions occur by processes other than physical entanglement. An additional use which can therefore be made of the 'shear-thinning' plot (η versus $\eta\dot{\gamma}^{0{\cdot}76}$) is to detect such interactions. For example, when the shear rate dependence of viscosity for xanthan solutions is plotted in this way, the graph shows pronounced curvature with, in particular, a sharp up-turn at low shear rates. Although the unusual behaviour of xanthan is obvious from a conventional double-logarithmic plot of η versus $\dot{\gamma}$, in other cases the departures from normal 'random coil' flow behaviour can be more subtle. The treatment proposed here, where viscosity is plotted on a linear, rather than a logarithmic scale, gives an extremely sensitive index of any such effects.

In earlier work (e.g. Morris *et al.*, 1981) the shear rate reference $\dot{\gamma}_{0\cdot 1}$ (i.e. the shear rate required to reduce η to $\eta_0/10$) was chosen. As discussed above, however, using a reference value of $\dot{\gamma}_{1/2}$ simplifies the shear-thinning equation by setting a constant multiplier to unity. Conversion between the two conventions [eqn (11)], however, is simple:

$$\dot{\gamma}_{0\cdot 1} = 18\dot{\gamma}_{1/2}.$$

Although developed for aqueous polysaccharide solutions, the generalised shear-thinning equation, and the linear plot derived from it, can be applied to solutions of any reasonably polydisperse 'random coil' polymer. Samples with a very narrow distribution of molecular weight cannot, however, be treated in the same way, since their shear-thinning behaviour is appreciably different: specifically, the terminal slope of double-logarithmic plots of η versus $\dot{\gamma}$ show significant departures from the value of $-0\cdot76$ implicit in the present analysis (Graessley, 1974).

As a further extension, the method can also be applied to small-deformation oscillatory measurements of dynamic viscosity (η^*). For simple fluids and solutions of 'random coil' polymers, the frequency-dependence of η^* is closely superimposable (Cox & Merz, 1958) on the shear rate dependence of steady-shear viscosity (η) at the same numerical values of frequency (ω/rad s^{-1}) and shear rate ($\dot{\gamma}$/s^{-1}). The results can therefore be analysed in the same way, by substituting η^* and ω for η and $\dot{\gamma}$ in eqn (8), and plotting η^* versus $\eta^*\omega^{0\cdot76}$.

The method works best for viscosities in the approximate range 10–95% of η_0. As discussed previously, the analysis becomes less reliable at very low shear rates, as η approaches η_0. The shear-thinning plot also becomes less reliable at very high shear rates, where η falls below $\sim 0\cdot1\eta_0$ (corresponding to the linear 'terminal' region in Fig. 1. This can be seen for the locust bean gum data (squares) in Fig. 3, where there is a noticeable downturn at high shear rates (high values of $\eta\dot{\gamma}^{0\cdot76}$). It should again be emphasised, however, that since the shear-thinning plots (Figs 2, 3 and 4) are linear on both axes, these discrepancies are tiny in comparison with the error involved in deriving equivalent information (η_0 and $\dot{\gamma}_{1/2}$) from a double-logarithmic plot of η versus $\dot{\gamma}$, and have negligible effect on the values of η calculated subsequently from eqn (8).

A final obvious qualification is that this generalised treatment of shear-thinning can be applied only to samples that do, indeed, shear-thin. At concentrations below the onset of coil-overlap and entanglement (i.e. below c*), solutions of 'random coil' polymers are virtually Newtonian (i.e. viscosity independent of shear rate), and significant shear-thinning occurs only at higher concentrations. This, however, is not a serious restriction since, for 'random coil' polysaccharides (Morris *et al.*, 1981), the viscosity at c* is ~ 10 mPa s (i.e. about ten times that of water), and thus the present treatment is relevant to almost all practical applications where higher viscosities are required.

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