Influence of the association of macromolecules in dilute solution on their reduced viscosity

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The influence of association on the reduced viscosity of macromolecules in dilute solution is calculated and a procedure to estimate the association constant is evolved. The theoretical results are compared with data in the literature.

INTRODUCTION

Generally, in reasonably dilute solution, a plot of reduced viscosity, $\eta_{sp}/c = (\eta - \eta_0)/\eta_0 c$, ($\eta$: viscosity of the solution, η_0: viscosity of the solvent) as function of the concentration c or of the specific viscosity η_{sp}, is a straight line, in accordance with the Huggins[1] law:

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

or the Schultz–Blaschke[2] law:

$$\eta_{sp}/c = [\eta] + k_H[\eta]\eta_{sp} \qquad (2)$$

respectively.

The parameters $[\eta]$ (intrinsic viscosity) and k_H (Huggins constant) obtained from equations (1) and (2) are nearly the same[3]. The intrinsic viscosity $[\eta]$ is a measure of the shape and size of the isolated macromolecule, the Huggins coefficient k_H, of their pairwise hydrodynamic interaction. For most random chain polymer systems $k_H \lesssim 0.5$[4]. There are 4 important exceptions to such straight lines:

(i) In cases where a systematic error $\Delta\eta_0$ was made in establishing the viscosity of the solvent. As a result there is a curvature, either convex or concave, depending on the sign of the error. The effect of the error will be most felt at low concentrations, i.e. at low values of η_{sp} since:

$$\Delta\eta_{sp}/\eta_{sp} = (\Delta\eta_0/\eta_0)[1 + 1/\eta_{sp}] \qquad (3)$$

where η_{sp} is the correct value based on η_0 and $\Delta\eta_{sp}$ the error resulting from the use of $\eta_0 + \Delta\eta_0$.

(ii) In cases of adsorption of the polymer onto the walls of the viscometer. This gives a concave curvature[5] very similar to the previous case.

(iii) In cases of polyelectrolyte solutions at low ionic strength. Here the dependence of η_{sp}/c on c is not steady[6] due to long range electrostatic repulsions.

(iv) In cases of association of macromolecules in solution. This results, as we shall see in the next sections, in a convex curvature and an effective Huggins coefficient $k'_H \gg 0.5$.

In recent years the association or aggregation of macromolecules in dilute solution has received renewed attention[7], perhaps because such processes may play an important role in biological systems[8] and in drag reducing solutions[9]. Due to the much higher value of the effective Huggins constant, as indicated by an earlier calculation of Simha[10], viscometric methods are very sensitive to aggregation[11,12]. In this paper we intend to evolve a standard procedure for the estimation of the aggregation parameters from the reduced viscosity vs. concentration curve. We shall treat two modes of association, dimerization and multimerization, the latter in a special case. These cases reduce to simple analytical expressions involving a minimum of assumptions and having no adjustable parameters.

We shall also give a quantitative interpretation in a few cases where experimental results are available and bring some corrections to two papers published earlier on this subject[12,13].

THEORY

General

The following calculations are restricted to dilute solutions, say to solutions of concentration such that[14] $\eta/\eta_0 \lesssim 1.6$, i.e.:

$$\eta_{sp} \lesssim 0.6 \qquad (4)$$

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The effect on the specific viscosity of a species j of macromolecules, present as the single solute component, in a concentration c_j (weight per volume), is given by:

$$(\eta_{sp})_j = [\eta]_j c_j + k_j [\eta]_j^2 c_j^2 \tag{5}$$

provided that it is valid to neglect higher order terms in $[\eta]_j c_j$. In the above $[\eta]_j$ is the intrinsic viscosity and k_j the Huggins constant for this species. If the solution consists of a mixture of several species i, their total contribution to the specific viscosity is:

$$\eta_{sp} = \sum_i [\eta]_i c_i + \sum_i k_i [\eta]_i^2 c_i^2 + \sum_{i \neq j} \sum_j k_{ij} [\eta]_i [\eta]_j c_i c_j \tag{6}$$

again assuming that higher than quadratic terms in concentration can be neglected.

This basic equation is different from one derived previously[13], which does not include the third term, representing the binary hydrodynamic interaction of the different species. Neglecting this term, however, leads to inconsistent results, as a very simple test will show: let us suppose that a mixture consists of n identical species of equal intrinsic viscosity and equal Huggins constant. Equation (6) should and indeed does, reduce to equation (5). Comparison of equation (6) (without the third term) and equation (5), however, leads to a Huggins constant k_H

$$k_H = k_j \left(\sum_i c_i^2 \Big/ \left(\sum_i c_i \right)^2 \right)$$

which is clearly incorrect.

Equation (6) can be simplified if $k_i = k_{ij} = k_H$ = constant. This is a fair assumption if the different molecules are of identical chemical structure and hydrodynamic behaviour. (The Huggins constant depends only slightly on the molecular weight[1,15].) One then finds:

$$\eta_{sp} = \sum_i [\eta]_i c_i + k_H \left(\sum_i [\eta]_i c_i \right)^2 \tag{7}$$

and

$$\eta_{sp}/c = \frac{1}{c} \sum_i [\eta]_i c_i + \frac{k_H}{c} \left(\sum_i [\eta]_i c_i \right)^2 \tag{8}$$

If the ratio $\gamma_i = c_i/c$ is independent of c, equation (8) is the basic equation for the calculation of the influence of polydispersity on specific viscosity. A comparison of (1) and (8) readily gives the average value $\langle[\eta]\rangle$ of the intrinsic viscosity of the polydisperse material:

$$\langle[\eta]\rangle = \lim_{c \to 0} \frac{1}{c} \sum_i [\eta]_i c_i$$

and we can write:

$$\eta_{sp}/c = \langle[\eta]\rangle + k_H (\langle[\eta]\rangle)^2 c \tag{9}$$

which agrees with experimental results[20].

Equations (7) and (8) are also the basic equations for the calculation of η_{sp}/c in the case of association, i.e. when c_i depends on c. To simplify the notation we define:

$$\langle \eta_{sp}/c \rangle = \left(\sum_i [\eta]_i c_i \right) / c \tag{10}$$

and write for equation (8):

$$\eta_{sp}/c = \langle \eta_{sp}/c \rangle (1 + c k_H \langle \eta_{sp}/c \rangle) \tag{11}$$

Note that $\langle \eta_{sp}/c \rangle$ still depends on c so that this equation, equation (11), is very different to equation (9). The value of k_H will have to be known or assumed before $\langle \eta_{sp}/c \rangle$ can be calculated, by means of equation (11), from the experimental data, η_{sp}/c and c.

Since:

$$[c k_H \langle \eta_{sp}/c \rangle] < [c k_H \eta_{sp}/c] = [k_H \eta_{sp}]$$

and $k_H \leqslant 0.5$ for coiled macromolecules we find using the criterion $\eta_{sp} < 0.6$ (equation (4)) that

$$c k_H \langle \eta_{sp}/c \rangle < 0.3 \tag{12}$$

in cases to which the above equations can be applied.

We shall now derive theoretical expressions for $\langle \eta_{sp}/c \rangle$ in the case of association. Two cases will be examined: the first is dimerization, where two species M_1 and M_2 are in equilibrium, according to the reaction

$$2M_1 \rightleftarrows M_2 \tag{13}$$

This case has already been studied by Simha[10], but gives a good introduction to the second case, that of linear multimerization for which we shall keep to nearly the same notation as that used previously[13]. The reactions are:

$$M_1 + M_1 \rightleftarrows M_2; M_2 + M_1 \rightleftarrows M_3; \ldots; M_{i-1} + M_1 \rightleftarrows M_i \tag{14}$$

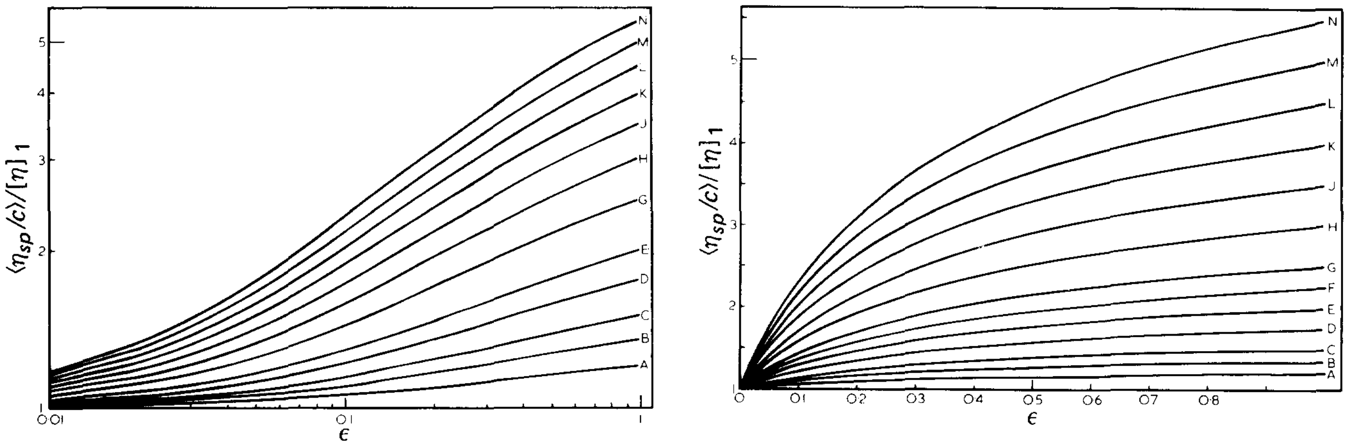
and we assume that the association constant K of the mass action law is the same for all these reactions. This is not an unreasonable assumption, but one which will have to be checked experimentally. Other simple relations between the association constants of the successive reactions (14) can also be treated analytically; for example $K_i = K_0 e^{-li}$ or $K_i = (i - 1/i) K_{i-1}$.

Dimerization

The mass action law applied to reaction (13) gives

$$[M_2] = K [M_1]^2 \tag{15}$$

where $[M_1]$ and $[M_2]$ are the molar concentrations of monopolymers of molecular weight M_1 and dipolymers of molecular weight $M_2 = 2M_1$, respectively. If c_i is the (weight per



Figures 1 and 2 Dimensionless reduced specific viscosity $\langle\eta_{sp}/c\rangle/[\eta]_1 = A$ *versus* dimensionless reduced concentration $Kc/M_1 = \epsilon$ with $r = [\eta]_2/[\eta]_1$ as parameter and equal to A, 1.4; B, 1.7; C, 2; D, 2.5; E, 3; F, 3.5; G, 4; H, 5; J, 6; K, 7; L, 8; M, 9; N, 10. Case of dimerization; A given by equation (19)

volume) concentration ($i = 1$ and 2), we can rewrite equation (15) as:

$$c_2 = 2Kc_1^2/M_1 \tag{16}$$

Solving this equation, given that the total concentration

$$c = c_1 + c_2 \tag{17}$$

we find that

$$c_1 = c[(1 + 8\epsilon)^{1/2} - 1]/4\epsilon \tag{18}$$

where

$$\epsilon = Kc/M_1$$

is a dimensionless parameter (reduced concentration). By substituting equations (18) and (16) in equation (10) it can be arranged to give

$$A = \{\langle\eta_{sp}/c\rangle/[\eta]_1\} = \left(\frac{(1 + 8\epsilon)^{1/2} - 1}{4\epsilon}\right) \times \left\{1 + [(1 + 8\epsilon)^{1/2} - 1]\frac{r}{2}\right\} \tag{19}$$

where

$$r = [\eta]_2/[\eta]_1$$

is the intrinsic viscosity ratio of dipolymer to monopolymer. The value of r would lie between 1.4 and 3.5, if according to the Mark–Houwink relation,

$$[\eta] = HM^a \tag{20}$$

and a lies between 0.5 (coil in a θ solvent) and 1.8 (rigid rod). Spheres dimerizing to give larger spheres have $r = 1$ and r can also be less than 1 if the dimer is considerably less asymmetric than the monomer. We have made numerical calculations up to values of $r = 10$. Such values might be attained if the association process would involve an intramolecular morphological change.

From equation (19) we recognize that by plotting the dimensionless quantity $A = \langle\eta_{sp}/c\rangle/[\eta]_1\rangle$ as a function of ϵ, a nest of curves can be obtained (depending only on the parameter r). The best way to compare experimental results with theory is to superimpose graphically log $\langle\eta_{sp}/c\rangle$ *versus* log c on a nest of curves of log A *versus* log ϵ with r as a parameter (*Figure 1*). The experimental curve is brought to optimum coincidence with one of the theoretical curves. Its r-value gives the experimental r-value, the vertical shift gives the value of $[\eta]_1$ and the horizontal shift the value of K/M_1.

If the data has been taken at sufficiently low concentrations, i.e. if $8\epsilon \ll 1$, equation (19) can be written as

$$\langle\eta_{sp}/c\rangle = [\eta]_1 + 2\epsilon[\eta]_1(r - 1); 8\epsilon \ll 1 \tag{21}$$

which is the relation obtained by Simha[10] but not by Priel and Silberberg[12] due to an error in the concentration units. The initial slope of η_{sp}/c *versus* c thus leads to the value of K, but measurements will have had to have been made at very low values of η_{sp}. From equation (19) it can also be seen that when $\epsilon \to \infty$, $\langle\eta_{sp}/c\rangle \to [\eta]_2$ but the convergence to the asymptotic value is very slow and the concentration at which the estimate of $[\eta]_2$ may be considered as acceptable is in the semi-dilute or even in the concentrated domain. Indeed, *Figure 2* shows that for values of $\epsilon \approx 1$ the asymptotic value of A, which should be r, is yet far from being reached.

Multimerization

The mass action law applied to reactions (14), gives:

$$[M_i] = K[M_{i-1}]\ [M_1] \tag{22}$$

So that

$$c_i = c_1\, i(Kc_1/M_1)^{i-1} \tag{23}$$

and

$$c = \sum_{i=0}^{\infty} c_i = /(1 - Kc_1/M_1)^2 \tag{24}$$

By solving equation (24) with respect to c_1 we have

$$c_1 = [1 + 2\epsilon - (1 + 4\epsilon)^{1/2}]\, c/2\epsilon^2 \tag{25}$$

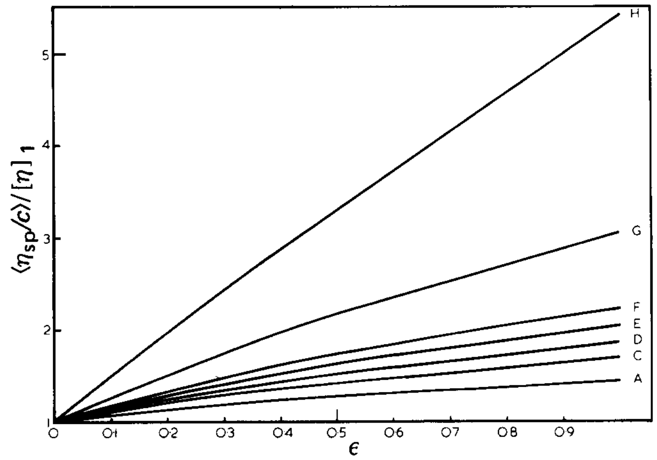


Figure 3 Dimensionless reduced specific viscosity $\langle\eta_{sp}/c\rangle/[\eta]_1 = A$ versus dimensionless reduced concentration $Kc/M_1 = \epsilon$ with a (Mark–Houwink exponent) as parameter and equal to A, 0.5; B, 0.6; C, 0.7; D, 0.8; E, 0.9; F, 1; G, 1.3; H, 1.8. Case of multimerization, A given by equation (28)

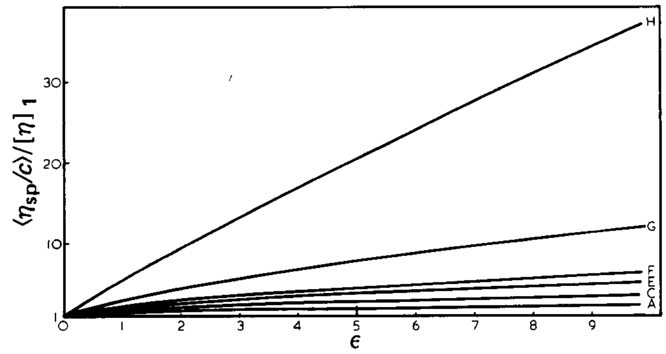


Figure 4 Dimensionless reduced specific viscosity $\langle\eta_{sp}/c\rangle/[\eta]_1 = A$ versus dimensionless reduced concentration $Kc/M_1 = \epsilon$ with a as in *Figure 3*. Case of multimerization; A given by equation (28)

and substituting equations (25) and (23) in (10) gives

$$A = \langle\eta_{sp}/c\rangle/[\eta]_1 = (1/\epsilon)\sum_{i=1}^{\infty}([\eta]_i/[\eta]_1)i \times [(1+2\epsilon-(1+4\epsilon)^{1/2}/2\epsilon]^i \qquad (26)$$

To make further use of this relation we have either to know all the parameters $[\eta]_i$ or make some assumption about them. Let us assume, therefore, that the parameters a and H of equation (20) are the same for all the species i, so that:

$$[\eta]_i = HM_i^a = i^a[\eta]_1 \qquad (27)$$

Since $r = [\eta]_2/[\eta]_1$, we find, using equation (27), that

$$a = \log r/\log 2$$

and that

$$A = \langle\eta_{sp}/c\rangle/[\eta]_1 = (1/\epsilon)\sum_{i=1}^{\infty} i^{1+a} \times [(1+2\epsilon-(1+4\epsilon)^{1/2}]/2\epsilon]^i \qquad (28)$$

which is easily computed and can be expressed analytically if a is an integer. Here again, the experimental results plotted as log (η_{sp}/c) *versus* log c, can be superimposed on a plot of log A *versus* log ϵ and the values of a, $[\eta]_1$ and K/M_1 obtained. The corresponding nest of curves with a as parameter (*Figures 3, 4* and *5*), however, differs significantly from that obtained for dimerization: the A vs. ϵ plots in this case are much less curved. It should be noted that the upper value of the Mark–Houwink exponent $a = 1.8$ used here corresponds to $r = 3.5$.

If $4\epsilon \ll 1$, we obtain the following approximate expression

$$\langle\eta_{sp}/c\rangle = [\eta]_1 + 2\epsilon[\eta]_1(r-1); 4\epsilon \ll 1 \qquad (29)$$

which (see equation 21) is the same relation as the one obtained for dimerization. Here, if measurements down to very low values of ϵ can be made, the initial slope gives the value of K/M_1, which can then be used to check other data.

Variation of the concentration of the different species with the total concentration

It is of interest to show how the concentration c_i of the species i varies relative to the total concentration c in these cases. We shall calculate the dependence of the dimensionless quantities $\gamma_i = c_i/c$ on ϵ.

Dimerization. The quantities γ_1 and γ_2 can be obtained from equations (17) and (18). It will be noticed (*Figure 6*)

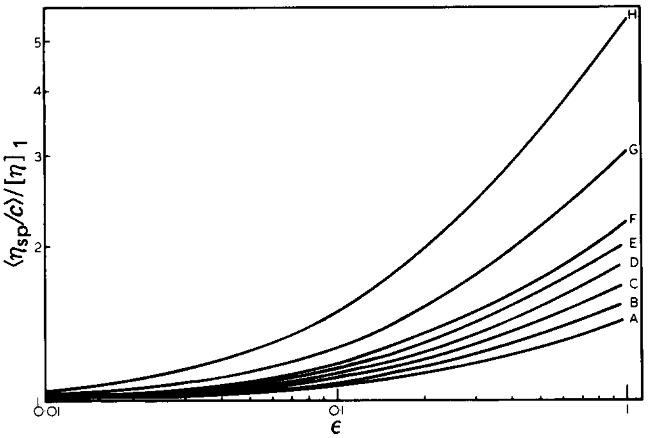


Figure 5 Dimensionless reduced specific viscosity $\langle\eta_{sp}/c\rangle/[\eta]_1 = A$ versus dimensionless reduced concentration $Kc/M_1 = \epsilon$ with a as in *Figure 3*. Case of multimerization; A given by equation (28)

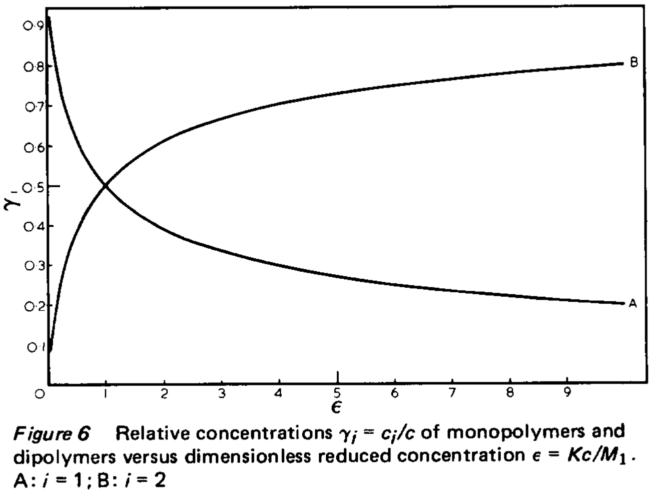


Figure 6 Relative concentrations $\gamma_i = c_i/c$ of monopolymers and dipolymers versus dimensionless reduced concentration $\epsilon = Kc/M_1$. A: $i = 1$; B: $i = 2$

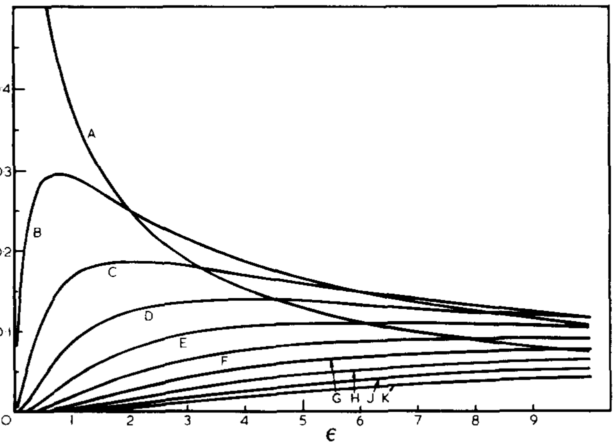


Figure 7 Relative concentrations $\gamma_i = c_i/c$ of associated species versus dimensionless reduced concentration. $\epsilon = Kc/M_1$. i = A, 1; B, 2; C, 3; D, 4; E, 5; F, 6; G, 7; H, 8; J, 9; K, 10

that the absolute values of their initial slopes is 2 and that $c_1 = c_2$ for $\epsilon = 1$. The relative concentration of the dimer in the mixture rapidly increases as ϵ increases.

Multimerization. Equation (25) gives:

$$\gamma_1 = c_1/c = [1 + 2\epsilon - (1 + 4\epsilon)^{1/2}]/2\epsilon^2$$

so that a plot of γ_1 vs. ϵ decreases steadily with an initial slope of (−2). From equation (23) we have:

$$\gamma_i = i\epsilon^{i-1}\gamma_1^i \tag{30}$$

and it is seen that each function γ_i, for $i > 1$, has a maximum:

$$\gamma_{im} = [4i/(i^2 - 1)]\,[(i - 1)/(i + 1)]^i$$

at

$$\epsilon_m = (i^2 - 1)/4 \tag{31}$$

which is such that:

$$\gamma_{im} \cdot i \xrightarrow[i \to \infty]{} 0.54 \tag{32}$$

This asymptotic value is reached to within 10% for $i > 2$. The initial slope is 2 for $i = 2$ and 0 for $i > 2$. *Figure 7* represents the variation of γ_i with ϵ. Though the range of ϵ is limited by equation (4), it can be seen from *Figure 7* that high order species may play an important role.

DISCUSSION

Limiting concentration

The above results are only valid at low concentrations, i.e. for concentrations c below a certain value c^*. η_{sp}^*, A^* and ϵ^* are then respectively the values of η_{sp}, A and ϵ when $c = c^*$. We have here assumed that:

$$\eta_{sp}^* = 0.6 \tag{34}$$

in the case of flexible chain macromolecules. For rods and ellipsoids $\eta_{sp}^* < 0.6$, the exact value depending on the aspect ratio[14]. From (34) we can write:

$$A = [\langle\eta_{sp}/c\rangle/[\eta]_1] < \eta_{sp}^*/c[\eta]_1 = \eta_{sp}^*K/\epsilon M_1[\eta]_1 \tag{35}$$

or

$$\log A < \log(\eta_{sp}^*K/M_1[\eta]_1) - \log\epsilon$$

When $c = c^*$, $\log A^* = \log\eta_{sp}^*K/M_1[\eta]_1 - \log\epsilon^*$

This is a straight line which defines the limit of the dilute domain for the nest of curves.

The effective Huggins constant

Substituting equation (21) or (29) into equation (11), assuming $8\epsilon \ll 1$ and developing up to the first order in c, we have

$$\eta_{sp}/c = [\eta]_1 + ck_H[\eta]_1^2 + 2Kc[\eta]_1(r - 1)/M_1;\ c \ll M_1/8K \tag{36}$$

and, by analogy with equation (1),

$$\eta_{sp}/c = [\eta]_1 + k_H'[\eta]_1^2c \tag{37}$$

with $k_H' = k_H + k_a$, where

$$k_a = 2K(r - 1)/M_1[\eta]_1 \tag{38}$$

The parameter k_H' is the effective Huggins constant, as measured close to zero concentration and is the sum of the 'natural' Huggins constant k_H and the 'additional' Huggins constant k_a. Experimentally k_a varies only slightly with molecular weight[16].

We shall now discuss the full relation, which from equation (8), can be written

$$\langle\eta_{sp}/c\rangle/[\eta]_1 = A + (2k_H/k_a)(r - 1)A^2\epsilon \tag{39}$$

with A given either by equation (19) or equation (26).

The role of the 'natural' Huggins constant

To show the extent to which $\langle\eta_{sp}/c\rangle/[\eta]_1$ depends on the value of k_H we have plotted $\langle\eta_{sp}/c\rangle/[\eta]_1$ vs. ϵ in *Figures 8* and *9* (for dimerization and multimerization respectively) for 3 values (2, 5 and 20) of the ratio k_a/k_H and for a few values of the parameters r and a respectively. The

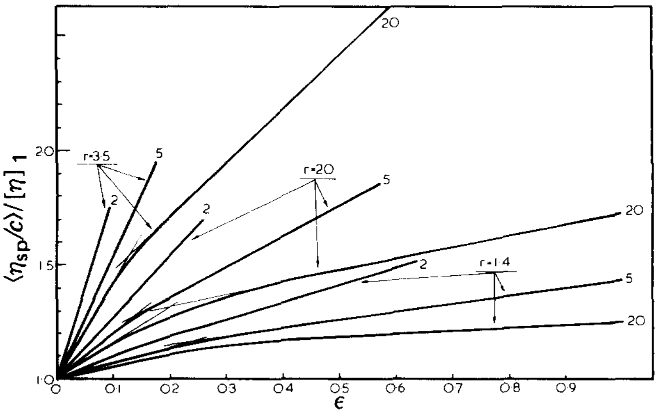


Figure 8 Dimensionless reduced specific viscosity (experimental) $\langle\eta_{sp}/c\rangle/[\eta]_1$ versus dimensionless reduced concentration $Kc/M_1 = \epsilon$. Case of dimerization with r = 1.4, 2 and 3.5 and with k_a/k_H = 2, 5 and 20. The curves are terminated at $\epsilon = \dot{\epsilon}^*$ for a flexible coil

plots terminate at the value ϵ^* corresponding to the limit of the dilute regime for a flexible chain macromolecule, i.e. when $(2k_H/k_a)(r - 1)A\epsilon = 0.3$. A comparison with *Figures 2* and *3* shows that the neglect of the 'natural' Huggins constant may introduce serious errors but only at values of $\epsilon > \epsilon^*/5$. For the lowest values of r and a, the plots can be approximated by 2 straight line segments (of which the upper one is well defined, and the lower one is a rough approximation); such plots (two straight segment Huggins plots) have been observed experimentally[16].

For a comparison of the experimental results with *Figures 1* or *5*, it is necessary first to select a value for k_H in what may have to be a rather arbitrary manner. For example, k_H may be put equal to that observed, at the same shear rate and in the same solvent, for a lower molecular weight fraction for which association does not exist. Similarly, if associations appear only above or below a certain critical shear rate[16], G_c, the value of k_H can be taken to be that observed below or above G_c respectively. Once k_H is chosen, $\langle\eta_{sp}/c\rangle$ can be obtained from the data by solving equation (11).

COMPARISON WITH EXPERIMENTS

In order to demonstrate the procedure we will discuss three sets of data in the literature[8,12,16].

Reisler *et al.*[8] have studied the multimerization of Bovine Liver Glutamate Dehydrogenase, a globular protein, in phosphate buffer by a variety of techniques[17] including viscosity[8]. From their results it appears that $[\eta]_1 = 3.2$ ml/g. Equation (11) was applied, putting $k_H = 0.4$, and $A = \langle\eta_{sp}/c\rangle/[\eta]_1$ was calculated. Comparing with the case of multimerization (*Figure 5*) gives the results shown in *Figure 10*.

A very good fit is obtained for $a = 0.7$ and $K/M_1 =$ 3200 ml/g. Reisler *et al.*[17] give a value for $K/M_1 = 2200$ ml/g based on a variety of equilibrium methods. Assembly in this case, however, has been shown to follow a more complicated pattern than the scheme (22) and the effect of the shear field is unclear since only two very similar shear rates were examined. Hence the absence of detailed agreement may be regarded as reasonable, particularly if (as in our next example) higher shear rates considerably favour multimerization.

Priel and Silberberg[12] have studied poly(methacrylic acid) (PMA) in 0.002 N HCl containing 4 mol % ethanol. The application of the procedure as described above leads to the results of *Table 1*.

The values indexed PS were those originally reported[12]. The value of r is very high but this can be explained by side to side association and the fact that the rate of shear dependence is high. The value $a = 1$ of the Mark–Houwink exponent is very satisfactory, the dimerized PMA probably being extended. The increase of K/M_1 and $[\eta]_1$ with G indicates that the association is favoured by increased shear rate in correspondence with the known anti-thixotropic behaviour of PMA.

The third example of an application of the above procedure concerns studies of polystyrene in decalin by Layec-Raphalen *et al.*[16]. Curves of η_{sp}/c vs. shear rate G in these cases show a convex curvature at high shear rates and can be approximated by two straight lines. For k_H we again take the value $k_H = 0.4$. This is the value observed in this polymer–solvent system at very high shear rates[18]. For example, at $G = 9800$ s^{-1} for a polystyrene of molecular weight $M = 3.7 \times 10^6$ (in decalin at 25°C) the following values can be deduced:

For dimerization: $[\eta]_1 = 175$ ml/g, $K/M_1 = 44$ ml/g, $r = 1.4$

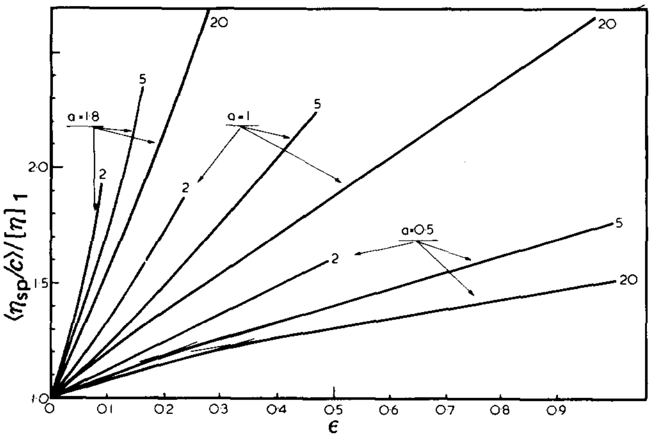


Figure 9 Dimensionless reduced specific viscosity (experimental) $(\eta_{sp}/c)/[\eta]_1$ versus dimensionless reduced concentration $Kc/M_1 = \epsilon$. Case of multimerization with $a = 0.5$, 1 and 1.8 and with $k_a/k_H =$ 2, 5 and 20. The curves are terminated at $\epsilon = \epsilon^*$ for a flexible coil

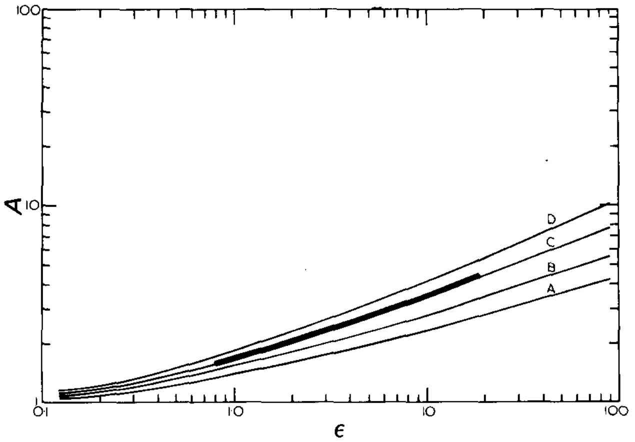


Figure 10 Dimensionless reduced specific viscosity A *versus* dimensionless reduced concentration ϵ. Case of multimerization with a = A, 0.5; B, 0.6; C, 0.7; and D, 0.8. Thick line drawn to fit the data of Reisler *et al.*[8] with $[\eta]_1 = 3.2$ ml/g and $K/M_1 = 3200$ ml/g

Table 1 Poly(methacrylic acid) (*MW* 63 000) in 4 mol % ethanol in 0.002N HCl at 30°C

	$G = 135$ sec^{-1}						$G = 215$ sec^{-1}					
	$[\eta]_1$ PS (ml/g)	$[\eta]_1$ (ml/g)	r	a	(K/M_1) PS (ml/g)	K/M_1 (ml/g)	$[\eta]_1$ PS (ml/g)	$[\eta]_1$ (ml/g)	r	a	(K/M_1) PS (ml/g)	K/M_1 (ml/g)
Dimerization	5.3	5	5	–	100	150	–	5.8	5	–	200	200
Multimerization	–	6.3	–	1	–	250	–	7.5	–	1	–	300

For multimerization: $[\eta]_1 = 175$ ml/g, $K/M_1 = 33$ ml/g,

$$a = 0.5$$

There is a fairly good agreement between the values of a and r and both correspond to what would be expected in a θ solvent, decalin at 25°C representing a medium close to θ conditions. Over the range of concentrations that were studied it is impossible to distinguish between multimerization and dimerization but at the highest shear rates (above 20 000 $\sec^{-1}$), the data fit the dimerization case only. The value of $[\eta]_1$ is the value of the intrinsic viscosity to be expected for such a molecular weight polystyrene molecule in the vicinity of the θ point.

CONCLUSIONS

In this paper we have considered the concentration dependence of the reduced viscosity of solute systems undergoing association. Dimerization and multimerization were studied assuming that the association constant and the particle topology remain independent of the degree of association. As a first step in the calculation an assumption about the hydrodynamic interaction parameter k_H has to be made.

A simple graphical comparison of the experimental results with the theoretical curves allows the determination of the association constant and of the intrinsic viscosity of the non-associated species. The experimental results have to be obtained at sufficiently low specific viscosities.

On the other hand results over a large range of concentrations (larger than one decade) are often required to distinguish between different processes of association. Unless association is strong and thus occurs in the dilute concentration range (where hydrodynamic interaction is confined to the Huggins coefficient term) the present analysis will not be of much value.

In particular it should be remembered that in many cases of association of open chain macromolecules one is converting intramolecular into intermolecular bonds and that rather complex considerations may be required to unravel the resulting shape and size changes.

The models treated here are rather specialized especially insofar as the dependence of $[\eta]_i$ on M_i is concerned. Their merit is that they lead to closed expressions. Good agreement between experiment and theory when it exists is thus very satisfactory but disagreement may merely imply that a more detailed analysis is required.

Within the scope of validity of the theory the dependence of the intrinsic viscosity and the association constant on the shear rate, on the temperature and on the thermodynamic quality of solvent should be further investigated. Since the association constant and the energy of association[10,19] are related, this may provide a good means for studying association in the shear field.

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