

# Equation of state for polymer solution

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Dedicated to Professor Imanishi on the occasion of his retirement

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## Abstract

The flow pattern through a cloud of polymer segments is obviously different from the flow pattern around a solid object. It can be shown theoretically, however, that the partial viscosity due to the cloud can take the same value as for a solid sphere with the radius of gyration of the cloud as its radius. The specific viscosity of polymer solution has been derived as  $2.5(c/c_1)$ , with  $c_1$  being the internal concentration associated with a polymer molecule. The internal concentration is the ratio of mass over the volume of gyration of segments in a polymer chain. A radius of gyration exists for any type of polymers, flexible or rigid, exhibiting different kinds of dependence on the molecular weight. From the expression of the specific viscosity, the intrinsic viscosity is shown to be equal to  $2.5/c^*$ ,  $c^*$  being the (minimum) internal concentration for the state of maximum conformational entropy. The equation for the specific viscosity, thus obtained, is expanded into a polynomial in  $c[\eta]$ . This formula is shown to agree with data for several kinds of polymers, with flexible, semi-rigid and rigid.

The quantity  $1/c_1$  can be interpreted as an expression for the chain stiffness. In polyelectrolytes, coulombic repulsive potentials affect the chain stiffness. The dependence of  $c_1$  on the effective population of polyions in the polyelectrolyte molecule is discussed.

An equation of state for the polymer solution is formulated that included the internal concentration. The virial coefficients emerge as a result of  $c_1$  not always being equal to  $c^*$ , and they are molecular weight dependent. © 2002 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

The Stokes–Einstein equation [1–3] is a description of how viscosity increases due to the presence of solid particles in a fluid. The specific viscosity  $\eta_{sp}$  is described in terms of the number,  $n$ , and volume,  $v$ , of the solid spheres suspended in unit volume of fluid with viscosity of  $\eta_0$ , i.e.

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = 2.5nv \quad (1)$$

The coefficient 2.5 has its origin in that the surface integral of the shear stress at the wall of the solid sphere is four times as great as the pressure drop across that sphere, and that the contribution to the overall viscosity from the pressure being equal to  $\eta_0/2$ . The value of 2.5 has been demonstrated experimentally by Eirich [4] with spherical beads suspended in liquid. Eq. (1) can be used as an empirical formula for particles that are not spherical, as long as they are randomly oriented, with  $v$  as an effective hydrodynamic volume resulting in the observed specific viscosity. A flow-induced

change in the orientation of the non-spherical particles would lead to a non-Newtonian viscosity, in which case a flow rate term would need to be included.

Flory and Fox [5] has shown that the specific viscosity for polymer solution in the dilute limit to be proportional to the cube of the RMS end-to-end distance,  $\langle r^2 \rangle^{1/2}$ , of the chain conformation, i.e.

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} = \Phi \frac{\langle r^2 \rangle^{3/2}}{M} \quad (2)$$

where  $M$  is the molecular weight of polymer.

Since  $cN_A/M$  is the number of molecules per unit volume of solution,  $N_A$  being Avogadro's number, Eq. (2) can be interpreted to mean the polymer molecule is hydrodynamically equivalent to the solid sphere of the diameter  $\langle r^2 \rangle^{1/2}$ . The Flory–Fox equation is further supported by the Mark–Houwink–Sakurada equation as applied to different solvents

$$[\eta] = K_{MHS} M^a \quad (3)$$

that the polymer molecule swells in a good solvent, so that the parameter  $\nu$  for  $M^\nu \propto \langle r^2 \rangle^{1/2}$  is greater than 1/2, and  $a$  becomes greater than 0.5. The term hydrodynamic volume

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has originated from the tacit assumption of Eq. (1) being applicable to the equivalent volume of a real polymer treated as if it were a solid sphere.

Empirical fit of these formulas notwithstanding a wriggling polymer molecules hardly resembles a solid sphere, hydrodynamically or otherwise. The equilibrium concentration for the unperturbed conformation is too low to behave as solid, e.g. it can be shown to be in the order of 1% for a chain with 10,000 beads. As the boundary layer thickness around each segment in the chain is in the order of the segment [8], it can be shown that the fluid can flow through the cloud of such segments. The streamlines *through* the cloud of chain segments are quite different from the streamlines that flow *around* a solid sphere. However, from the theory of Kirkwood and Riseman [9], the specific viscosity due to the radial distribution of polymer segments in suspension can be calculated, and the intrinsic viscosity for the flexible chain is essentially the Flory–Fox equation shown earlier.

It will be shown by our analysis that the flow around a solid sphere with the radius that is equal to the RMS radius of gyration for any type distribution of segments in a chain (or a rod) will exhibit the same value of specific viscosity as for the flow through the cloud of the polymer chain in solution. Thus the volume with the radius of gyration can be treated as the empirical hydrodynamic volume for the specific viscosity.

The concept of hydrodynamic volume could be extended beyond the ideal dilute solution [6] to the concentration-dependent specific viscosity. The Huggins [7] equation is a first order modification of the term  $c[\eta]$ , and a polynomial expansion in  $c[\eta]$  had been proposed to account for higher order effects of concentration.

The Einstein–Stokes equation for the specific viscosity is not a constitutive equation. If the intrinsic viscosity were a measure of the energy loss in the fluid that goes around a solid ball of polymer molecule, then it would have nothing to do with the frictional dissipation of motion as polymer molecules snake through the solution. If, on the other hand, the intrinsic viscosity is in fact a measure of the frictional loss in fluid that flows through the cloud of segments, then the intrinsic viscosity has much to do with viscometric behavior. The structural parameters related to theory of worm-like motion proposed by Kratky and Porod [12], theory on the characteristics of molecular structure as related to the viscosity by Yamakawa [13,14], and theories introduced with in-depth review by Fujita [15], all are related to the structure that can be analyzed from the intrinsic viscosity. Theories utilizing the worm or tube concept [16,17] are embedded in the context of an environment surrounded by neighboring polymer molecules, and the radius of gyration of parts of a chain is utilized to characterize it. The coordinated movements of parts of a chain and among chains as theorized by Rouse [10] and Bueche [11] theories are indirectly related because the molecular interpretation of viscoelasticity utilizes the same molecular parameters.

## 2. Theory

We place a wriggling polymer chain in a parallel uniform flow field, flowing in the  $x$ -direction. At a far away distance from the center of the cloud in the  $y$ -direction, the velocity gradient  $dV/dy$  is zero. Moving closer to the cloud's center, the velocity decreases as the fluid is met by more densely populated segments. The dependence of  $dV/dy$  on  $y$  (or  $r$ ) direction inside the cloud of segments can be formulated by considering the concentric shells, each containing one bead, such that the specific viscosity increases by  $2.5(4\pi r_j^2)\Delta r_j$  for the  $j$ th layer of thickness  $\Delta r_j$ , with the  $j$ th bead to be counted from the center. The distance  $r_j$  denotes the distance from the center of the cloud to the  $j$ th bead. By summing  $4\pi r_j^2\Delta r_j$  from  $j = 1$  through  $N$  ( $N$  is the total number of beads in the chain) and averaging them for all existing individual polymer molecules with different conformations, will obtain the volume of gyration

$$\sum_j^N 4\pi r_j^2 \Delta r_j = \frac{4\pi}{3} \langle s^2 \rangle^{3/2}$$

which is multiplied by 2.5 to obtain  $\eta_{sp}$ . Compared to this, a solid sphere with radius  $R$  in its place will obtain  $\eta_{sp}$  of  $2.5 \times 4\pi R^3/3$ . Thus the concluding statement can be made that “A cloud with the radius of gyration of  $\langle s^2 \rangle^{1/2}$  will render the same specific viscosity as the solid sphere with radius  $R$  that is equal to the  $\langle s^2 \rangle^{1/2}$  of that cloud”. The average internal concentration  $c_1$  can be defined by the equation:  $c_1 = (M/N_A)/(4\pi \langle s^2 \rangle^{3/2}/3)$ , where  $M$  is the molecular weight of the polymer for the cloud.

Since there are  $N_A c/M$  number of clouds per unit volume of solution, each with the effective volume of  $4\pi \langle s^2 \rangle^{3/2}$ , the specific viscosity is obtained:

$$\eta_{sp} = 2.5 N_A \frac{4\pi}{3} \langle s^2 \rangle^{3/2} \frac{c}{M} \quad (4)$$

## 3. The intrinsic viscosity

The intrinsic viscosity is defined as the dilution limit of the specific viscosity over  $c$ . This is the state of ideal dilute solution, in which the conformational probability is at its maximum, unperturbed by the presence of neighbor molecules, and the cloud's volume is also at its maximum. From the specific viscosity of Eq. (4), the intrinsic viscosity  $[\eta]$  is obtained

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} = 2.5 N_A \frac{4\pi}{3} \frac{\langle s^2 \rangle^{3/2}}{M} \quad (5)$$

which is readily identified with the Flory–Fox equation, Eq. (2), if a  $\langle s^2 \rangle^{1/2}$  is proportional to  $\langle r^2 \rangle^{1/2}$ , which is true for flexible chain  $\langle s^2 \rangle^{1/2} = \langle r^2 \rangle^{1/2}/\sqrt{6}$ . The experimentally obtained Flory constant,  $\Phi$  in Eq. (2), has been quoted [5] as  $2.1 \times 10^{23}$  for several flexible chain polymers. If this value is assumed, then  $\langle s^2 \rangle^{1/2}$  in Eq. (5) should be about

one-third of  $\langle r^2 \rangle^{1/2}$ , which is close to the value of  $\langle r^2 \rangle^{1/2}/\sqrt{6}$ . Derivation of Eq. (5) did not assume any restrictions on the types of polymer chain, such as flexible or stiff chains. In fact, all these variables, including excluded volume effects and non-theta solvents effects, are included in the value of  $\langle s^2 \rangle^{1/2}$ . The Flory constant, on the other hand, would not be constant for different polymers that have a different relationships between  $\langle r^2 \rangle^{1/2}$  and  $\langle s^2 \rangle^{1/2}$ , e.g. a rigid or semi-rigid straight chain, or some non-uniform effects of excluded volume. But the proportionality constant of Eq. (5) for  $\langle s^2 \rangle$  should remain constant, as it should be independent of the structure.

For flexible chain polymers, the radius of gyration  $\langle s^2 \rangle^{1/2}$  is proportional to  $M^{1/2}$  in the theta condition, but in good solvent the cloud volume expands, so  $\langle s^2 \rangle^{1/2} \sim M^{1/2} \alpha$  with  $\alpha$  being the expansion factor. The expansion  $\alpha$  is molecular weight dependent, so  $\langle s^2 \rangle^{1/2} \sim M^\nu$  in general. The Mark–Houwink–Sakurada equation, Eq. (3), follows directly from Eq. (5), with the value of  $a$  in the MHS equation to be equal to  $3\nu - 1$ . In a good solvent, the cloud swells because more solvent molecules are taken inside the cloud. Values of  $a$  and  $K_{\text{MHS}}$  for the M–H–S equation can be found for various polymers in Polymer Handbook [18].

Patel and Takahashi [19] have obtained the values of  $K_{\text{MHS}}$  and  $a$  for *cis*-polyisoprene in hydrocarbon solvent as  $1.94 \times 10^{-2}$  and 0.70, respectively, in the molecular weight range higher than  $4 \times 10^3$ . For molecular weight below  $10^3$ , however, the value of  $a$  was reported to be 1.2. Polyelectrolyte solutions with abundance of added salt ions are known to behave as usual polymers with no polyions, such as the viscosity being proportional to  $\sim M$  for low molecular weight but to  $\sim M^3 - M^4$  for high molecular weight [20]. The salt ions act as shielding the polyions, which would render the polyelectrolytes the behavior so different from ordinary polymers. Hyaluronan is no exception [21,22] when with salt concentration of greater than 0.1 M NaCl. Experimental data of our own on the salt-shielded hyaluronan [23,24] revealed that there are also two kinds of molecular weight dependence for the intrinsic viscosity, each with its own set of  $K_{\text{MHS}}$  and  $a$ . In the high molecular weight range,  $K_{\text{MHS}}$  of  $2.9 \times 10^{-2}$  and  $a$  of 0.80 were observed, whereas in the low molecular weight range,  $K_{\text{MHS}}$  of  $6.54 \times 10^{-4}$  and  $a$  of 1.16 were observed. The value of 0.8 for the power  $a$  for the MHS equation for the high molecular weight is observed frequently, which is easily understood for chains of random conformations in good solvents. The value of 1.16, found in the low molecular weight range, however, would imply a different molecular weight dependence for the radius of gyration. The two sets of similar values for  $a$  have also been reported for the hyaluronan in salt solution [25–32] for large molecular weight.

The stiffness of a chain is determined by, among other things, the difference in free energy between the straight and flexed conformations, e.g. the *trans* and *gauche* conformations. For a chain of given stiffness, if the molecular length

is very short, the ratio of the arc to the chord is closer to unity so the chain is nearly straight. For a straight chain, the end-to-end distance is proportional to the molecular weight, as against  $M^{1/2}$  or  $M^\nu$  for the longer molecule of the same kind of polymer. A straight chain can rotate around an axis through the center at various angles of inclination. Such a rotating rod can result in a cloud of very different kind. The mean square radius of a stiff rod, consisting of  $N$  segments each with length  $\ell$ , is  $\langle s^2 \rangle = N^2 \ell^2 / 12$ . The lateral thickness of the rod is designated as  $\delta$ . So the *characteristic volume* is obtained by integrating  $\delta \pi \{N^2 \ell^2 / 12\} \sin^2 \theta d\theta$  for all angles of inclination,  $\theta$ , which obtains  $\delta \pi^2 N^2 \ell^2 / 24$ . Thus, the intrinsic viscosity in Eq. (5) would depend on  $N^2/M$ , i.e. it would be proportional to  $M$  (or slightly higher in good solvent with  $a$  of 1.2). These two extreme regimes of molecular weight dependence for the intrinsic viscosity have been recognized by Peterlin [33], and also by Kuhn and Kuhn [34], who introduced the equation

$$[\eta] = \frac{AN}{1 + BN^{1/2}} \quad (6)$$

to cover the both regimes of molecular weight. It is seen in this equation that, for small  $N$ ,  $[\eta]$  is proportional to the molecular weight, while with high molecular weight it is proportional to  $N^{1/2}$ . This behavior at low values of  $N$  is consistent with the original discovery by Staudinger [35] of the proportionality between viscosity and molecular weight in a series of (low molecular weight) paraffins. The relative values of constants  $A$  and  $B$  in Eq. (6) determine the critical molecular weight that separates the two ranges of behavior. The ratio  $A/B$  is therefore a measure of stiffness. The critical molecular weight, thus found, of  $3.75 \times 10^4$  for the hyaluronan, and  $4 \times 10^3$  for the polyisoprene, can be shown to represent the molecular length at which the contour length is equal to about  $\pi \langle r^2 \rangle^{1/2}$ , obtained by assuming the Flory parameter of  $2.1 \times 10^{23}$ .

#### 4. Chain stiffness

Like many jargons, the word ‘stiffness’ could mean a different thing depending on the context. In the present context, it is that of an entropic spring. As such, the stiffness could mean the tendency to be straight, or could be translated to  $\pi \langle s^2 \rangle^{1/2} / N\ell$  where  $N\ell$  is the contour length of the chain. This is not the mechanically defined resistance to a bending stress, which typically arises from raising the intermolecular potential energy, rather than lowering the entropy, in deforming the body.

We have pointed out that, in the dilution limit, the volume of gyration of a polymer, with given molecular weight, would be at maximum, and that the internal concentration  $c_1$  is at minimum, as this state of dilution represents the unperturbed (by neighbors) conformations. If the volume of gyration is expanded, e.g. in a good solvent, then  $c_1$  would decrease further. The expansion, in general, is a result

of the more intense interaction between solute and solvent molecules, as in the above case, or of the tendency for the solute segments to avoid the like segments more than they would the solvent molecules. An example for the latter would be found in polyelectrolytes in the absence of added salt that would shield the polyions from acting on each other.

Polyelectrolytes are polymers with ionic groups. Those polyions will exert mutual coulombic repulsion potential. So the polyelectrolytes have the tendency to swell with more polyions in the solution. We let the radius of gyration to expand from  $\langle s^2 \rangle^{1/2}$  without polyions to  $\langle s_p^2 \rangle^{1/2}$  with unshielded polyions. For a given polymer, the polyions are placed at regular intervals along a molecule. The population of the polyions in a cloud would be proportional to  $c_1$  without polyions, or inversely proportional to  $\langle s^2 \rangle^{3/2}$ . The presence of polyions will expand the radius of gyration from  $\langle s^2 \rangle^{1/2}$  to  $\langle s_p^2 \rangle^{1/2}$ , but the polyion population itself is proportional to  $\langle s^2 \rangle^{1/2}$ , so  $\langle s_p^2 \rangle^{3/2}$  is proportional to the square of  $\langle s^2 \rangle^{3/2}$ , which is  $\sim M^3$ , and the proportionality of the intrinsic viscosity to  $M^2$  is predicted as  $\langle s_p^2 \rangle^{3/2}/M \sim M^3/M$ . The value of 2 for the Mark–Houwink–Sakurada's power  $a$  has been observed in many polyelectrolytes in solutions without added salt [18].

## 5. At higher concentration

When the concentration is increased, the conformational probability would become more restricted, and  $c_1$  increases. (The conformational probability in the broad sense should include the probability for the location of the center of mass of the chain that keeps traveling in the solution, as it is for the non-polymeric molecules in the gaseous state). So the decrease in entropy begins from zero concentration.

By substituting  $c_1$  into Eq. (4), the specific viscosity is written in terms of  $c/c_1$ , which is the volume fraction of the clouds in solution:

$$\eta_{sp} = 2.5 \frac{c}{c_1} \quad (7)$$

This equation is general for all concentrations, as  $\langle s^2 \rangle^{1/2}$  is concentration-dependent. The internal concentration is at minimum for  $c \rightarrow 0$ , which corresponds to the unperturbed (maximum) conformational probability, and is defined as  $c^* = c_{l,\min}$ , so the intrinsic viscosity is obtained

$$[\eta] = 2.5/c^* \quad (8)$$

and Eq. (7) can be written in terms of  $[\eta]$ ,

$$\eta_{sp} = c[\eta] \frac{c^*}{c_1} \quad (9)$$

To evaluate the specific viscosity from Eq. (7) or (9),  $c_1$  will have to be evaluated in terms of  $c$ . To do this, the concentration dependence of conformational entropy would have to be evaluated. The exact evaluation is a difficult task;  $c_1$  remains nearly constant at  $c^*$  until  $c$  exceeds  $c^*$ , then

increases with  $c$  towards higher concentration. We will instead introduce an approximate expression for Eq. (7) in terms of  $c[\eta]$  that is an experimentally obtainable value. Taking derivative of  $c/c_1$  with respect to  $c$  obtains,  $d(c/c_1)/dc = 1/c_1 - (c/c_1^2)d(c/c_1)/dc$ . Ignoring the second term as insignificant (this is essentially assuming a constant coefficient for  $c/c_1$  in  $c$ , similar to the constant values for the constant compressibility) then,  $[d(c/c_1)/dc]\Delta c \approx \Delta c/c_1$ . For  $\Delta c$  from 0 to  $c$ ,  $d(\ln c/c_1)dc \approx 1$ . Setting  $K_H = 0.4$ , arrived at from the value of 2.5 originating in Eq. (1), and with boundary condition that  $c \rightarrow 0$ ,  $c_1 = c^*$ , it is obtained

$$\frac{c}{c_1} = K_H \eta_{sp} \approx K_H c[\eta] \exp(K_H c[\eta]) \quad (10)$$

which is expanded, and obtains

$$\eta_{sp} \approx c[\eta] \left\{ 1 + K_H c[\eta] + \frac{1}{2!} (K_H c[\eta])^2 + \frac{1}{3!} (K_H c[\eta])^3 + \frac{1}{4!} (K_H c[\eta])^4 + \frac{1}{5!} (K_H c[\eta])^5 + \dots \right\} \quad (11)$$

Eq. (11) is Martin's equation, and it is known to deviate from the experimental data at high  $c[\eta]$  values [40].

For example, Eq. (11) is compared with data obtained by Berriaud, Milas, and Rinaudo [39] expressed with an empirical expression

$$\eta_{sp} = c[\eta] + 0.42(c[\eta])^2 + 7.77 \times 10^{-3}(c[\eta])^{4.18} \quad (12)$$

demonstrating the departure for Eq. (11) from the data at  $c[\eta]$  above 10.

Each term in Eq. (11) can be interpreted as resulting from overlap of the associated volumes for one, two, three, etc. molecules. When the concentration is very low, the lack of opportunity for a molecule to touch another would limit the overlap to between two molecules. This would correspond to taking only the first two terms in the bracket in Eq. (11), and we obtain the Huggins equation, with  $K_H$  clearly the Huggins constant, and it is 0.4 as a consequence of  $1/2.5$  from the Einstein–Stokes constant in Eq. (1). Experimental values for  $K_H$  have been reported, ranging between 0.3 and 0.5, in the compilation for many kinds of polymers by Stickler and Sutherland in Polymer Handbook [18]. The values for hyaluronan, obtained by Shimada [27], were reported typically from 0.35 to 0.40 in the high molecular weight range. For polyisoprene in a hydrocarbon solvent, the value of 0.42 was reported [19].

The infinite number of terms in Eq. (11) assumes possibilities for overlap up to among all molecules in the solution, clearly an overestimation of the neighbor contacts. If we choose a more realistic number of four for the neighbors in touch, as a tetrahedral packing of spherically symmetrical bodies, then we would obtain a polynomial with first four terms of Eq. (11), as

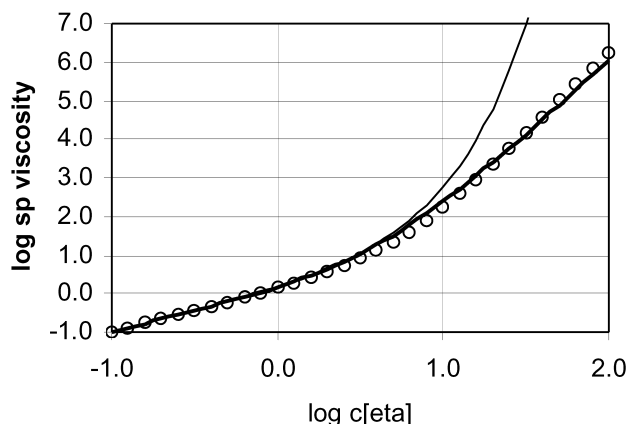


Fig. 1. Comparison of Eq. (11) (—) Eq. (13) (---) and data (O) [39] for hyaluronan in the 0.5 M NaCl solution.

described by Eq. (13) below (Fig. 1):

$$\eta_{sp} \cong c[\eta] \left\{ 1 + K_H c[\eta] + \frac{1}{2!} (K_H c[\eta])^2 + \frac{1}{3!} (K_H c[\eta])^3 \right\} \quad (13)$$

This equation, again with the value of 0.4 for  $K_H$ , fits well not only for the data shown above, but for data for various kinds of polymers. This is shown in Fig. 2 in which, in addition to Berriaud et al.'s data on hyaluronan, the data on polyisoprene in hydrocarbon solvent obtained by Patel and Takahashi, the data on polystyrene, polyisoprene, polybutadiene by Raspaud et al. [41], the data on semi-rigid polyhexyl isocyanates by Ohshima et al. [42], and the data on straight and rigid polyphenylenes by Kwei et al. [43] have been compared with Eq. (13). The fit with is excellent with all these polymers. In all these data, we fitted Eq. (13) directly to raw data, through trial and error with the values of  $K_H[\eta]$  for the best fit, rather than going through the often practiced procedure of first determining the values for  $K_H$  and  $[\eta]$  by drawing the straight lines for Huggins and Kraemer equations against  $c$  for a low concentration range. In other words, in our procedure, we treated

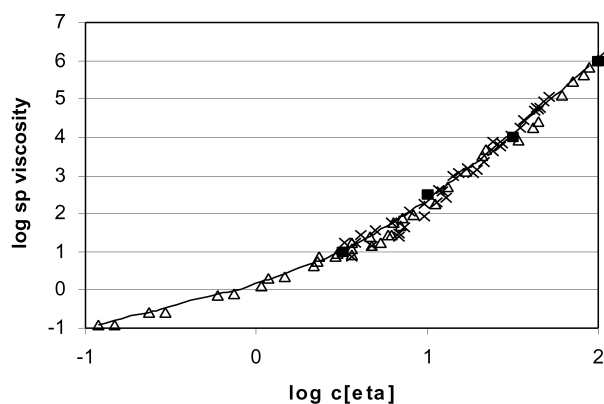


Fig. 2. Comparison of Eq. (13) (—) with experimental data for rigid (×), semi-rigid (■), and flexible (Δ), polymers.

$K_H[\eta]$  to be a single variable, with  $K_H = 0.4$ , and curve-fitted the data directly with Eq. (13) against  $c[\eta]$ . Raspaud et al. [41] had concluded by their procedure of analysis that the specific viscosity could not be a function of  $c[\eta]$  only; their analysis led to the  $\eta_{sp}$  vs.  $c[\eta]$  plots to diverge for different molecular weight, while our analysis of their raw data has led to a good fit with Eq. (13) for all molecular weight values. We experienced, on different occasions, that a systematic error could be generated in  $K_H$  and  $[\eta]$ , if the data in low  $c$  regions were approximated by straight lines, that these errors tend to lead to greater values of  $K_H$  for greater  $M$ . With our procedure, on the other hand, Eq. (13) has worked well for variety of polymers, including a polyelectrolyte solution with added salts.

We have earlier commented briefly on the effect of polyions on the intrinsic viscosity of polyelectrolyte solution when no salt is added to shield polyions' electrostatic potential [36]. The increased concentration of the polymer will increase the concentration of the polyions, which in turn will increase  $\langle s^2 \rangle^{1/2}$  to  $\langle s_p^2 \rangle^{1/2}$  because of coulombic repulsion among the polyions. Milas et al. [21] have reported that the electrostatic interactions in ionic polysaccharides increased the persistence length, which supports the above argument.

There is another peculiar concentration effect in polyelectrolytes at very low polymer concentrations. The apparent intrinsic viscosity will increase when the concentration is *decreased*, i.e.  $\eta_{sp}/c$  is inversely proportional to the square root of  $c$ , according to Fuoss's empirical equation [37]. The mechanism for this phenomenon was made clearer in the form reworked by Stivala and coworkers [38] in which the term  $c[\eta]$  in Huggins' equation was replaced with  $[\eta]/c^{1/2}$ . At very low polymer concentrations, the polyions in neighboring molecules become further removed, while the repulsive effect from those ions on the same molecule remain unchanged. The net effect of the *intramolecular* repulsive potential becomes more pronounced at these extremely low concentrations. The chains become straighter, and  $\langle s_p \rangle^{3/2}$  further increases as concentration is decreased beyond the already expanded state. The expansion is inversely proportional to  $M^{3/2}$ , but the number of polyions is proportional to  $M$ , so it is  $\sim c^{-3/2}$ . Thus  $c[\eta]$  is now modified to  $\{c[\eta]\}/c^{3/2} = [\eta]/c^{1/2}$  in agreement with Stivala's formula.

In support for this hypothesis of 'stiffening' the unshielded polyelectrolyte chains further at the very low concentration, we cite the unpublished data [46] on the rigid polyphenylenes with ionic substituent groups that showed no Fuoss effect. This is because, in this case, the chains were already fully extended, as the paraphenylene conformers are co-linear, and their rotation does not affect the conformation and the  $\langle s^2 \rangle^{1/2}$  remains constant.

Lastly on the effect of polyions on viscosity, we have not discussed the lubricating effect that polyions might play while the polyelectrolyte solution flows against a wall

containing the polyions with similar electrostatic charge. For example, red blood cells covered with polysaccharides with negatively charged polyions apparently behave slippery in flowing past each other [47]. The repulsive nature between polyions with the same kind of charges will help keep them separated from the wall, greatly reducing the friction. This is perhaps the most important *in vivo* behavior of biological polyelectrolytes that may not be observed *in vitro* experiments and, unfortunately, could not be included in the present analysis because we are unable to find relevant data.

## 6. Equation of state

The thermodynamic state is described by the free energy dependence on the intensive and extensive quantities. The Gibbs free energy  $\Psi$  for the gaseous state is given by

$$\Psi = U + pV - TS \quad (14)$$

where  $U$  is the internal energy,  $p$  the pressure,  $V$  the volume,  $T$  the temperature, and  $S$  the entropy. In the ideal gas, where intermolecular potential remains constant,  $pV$  is in balance with  $TS = RT$ , i.e.

$$pV = RT \quad (15)$$

per mol.

In the solution, the solute molecules are distributed in the space of solvent, undergoing Brownian motions. The osmotic pressure  $\pi$  is the partial pressure resulting from the kinetic motion of solute molecules on the semi-permeable membrane. The molar volume is the space in which the solute molecules are evenly distributed, so it is equal to the inverse of the molar concentration, or  $1/(c/M) = M/c$ , with  $M$  the molecular weight of solute. The equation that corresponds to Eq. (15) would be  $\pi(M/c) = RT$  or rearranging, van't Hoff's equation is obtained,

$$\frac{\pi}{cRT} = \frac{1}{M} \quad (16)$$

For the polymer, it would be an ideal solution only if  $c_1 = c^*$  at all concentrations. In general,  $c_1 \neq c^*$ , and

$$\frac{\pi}{cRT} = \frac{1}{M} \frac{c^*}{c_1} \quad (17)$$

The right side is expanded in a similar way that Eq. (13) was arrived at

$$\frac{c^*}{c_1} = \exp\left(\frac{c}{c^*}\right) \quad (18)$$

to obtain the polynomial with the limited number of terms for the same reason,

$$\frac{\pi}{cRT} \approx \frac{1}{M} \left( 1 + \frac{c}{c^*} + \frac{1}{2!} \left(\frac{c}{c^*}\right)^2 + \frac{1}{3!} \left(\frac{c}{c^*}\right)^3 \right) \quad (19)$$

This equation may be compared with the equation:

$$\frac{\pi}{cRT} = \frac{1}{M} + A_2c + A_3c^2 + A_4c^3 \quad (20)$$

It is noted that the virial coefficients are dependent on the molecular weight  $M$ , as  $c^* \sim M^{-a}$  for flexible chains. For example,  $A_2$  would be  $M^{-0.2}$  if  $a$  is assumed to be 0.8, as it is common to solution in a good solvent [48].

When two states can exist at the same temperature, a phase transition can occur. The most common phase transition is the fusion/crystallization at a temperature at which  $U - TS$  is the same for the solid and liquid phases. For the case such as described by Eq. (17), two states are possible at the same concentration with different internal concentrations. The latter can be realized by, for example, changing the radius of gyration by changing the salt concentration for polyelectrolyte solution, or by changing the molecular weight of the polymer. There are many ways for phase changes or pseudo-phase changes can occur without invoking a change in internal energy. Some liquid crystals can form even when there is no change in intermolecular potential during the formation, i.e.  $\Delta U$  is nearly zero per Fraden [44] in accordance with the theory of Onsager [45].

We did not choose the comprehensive ways of formulating the osmotic pressure that includes not only the entropy but also the heat of dissolution, as illustrated by Billmeyer [49] earlier and by Cassasa and Berry [50] in more recent years. The use of Flory Huggins does not involve the internal concentration, which we feel is an important parameter to connect the concentration-dependent (osmotic) pressure. By our approach, we illustrated the purely entropic phase transition through concentration change, and also the polymer-specific virial coefficient that is related to the entropy decrease by the increase in internal concentration.

## 7. Concluding remarks

The solution state has been described that depends on the average internal concentration for the group of permanently unevenly distributed particles or segments. The concentration dependence of the specific viscosity was introduced by considering the dependence of the internal concentration on the overall average concentration of the solution. From the analysis the viscosity can be shown to be proportional to  $M$  at low  $c[\eta]$  and rises finally to  $M^3$  or  $M^4$  at high  $c[\eta]$  regions. The concentration dependence of the critical molecular weight that separates the two behaviors agrees with data, but the 'entanglement' concept, often modeled intuitively by the temporary cross-linked network by Green and Tobolsky [51], or by the train of molecules pulled by a molecule modeled by Bueche [11] seems unrelated to the phenomenon analyzed here, particularly because the same equation applies to rigid rod-like molecules. It seems to be, rather, directly related to the concentration dependence of the internal concentration for dynamic molecules.

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