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Several articles over the past decades have reported a peak in the curve of reduced viscosity η_r vs polyelectrolyte concentration Cp when diluted with pure water or a fixed, low ionic strength solution. The current article shows that the large changes in conformation which accompany changes in ionic strength C_s, for long, linear, semiflexible polyelectrolytes, and which enter in the first, quadratic interaction term of the solution viscosity, are sufficient to account for the existence, relative magnitudes, and positions of peaks in such viscosity profiles. This is illustrated for hyaluronic acid (HA), for which the variations of radius of gyration with ionic strength have been previously determined experimentally. The conformational interpretation predicts that in the coil limit, the position of the viscosity vs Cp peak is independent of mass, but that its height should be roughly proportional to M at fixed Cs, and to roughly $CpCs^{-1.5}$ for a fixed M. The explanation is meant as a limiting case for long, linear polyelectrolytes and posits that steric, or hard, interactions between separate polymers dominate over electrostatic interactions when the polyelectrolyte dimensions are much larger than κ^{-1} the electrostatic screening length. The other extreme, short, chain polyelectrolytes and other inextensible objects, such as spheres, are mentioned in light of previously elaborated theories based on interacting electrostatic atmospheres when the dimensions of such objects are smaller than κ^{-1}.

INTRODUCTION

Over the years, a number of articles dealing with polyelectrolyte solutions have appeared which report the existence of a peak in reduced viscosity η_r vs the polymer concentration Cp when the solution is diluted with pure water or a low ionic strength stock. Such behavior has been demonstrated for a number of semiflexible linear polyelectrolytes, e.g., hyaluronate[1,2] (HA), carboxy-methyl cellulose,[3] thymonucleate,[4] gum arabate,[5] poly(4-vinylpyridine),[6] poly(2-vinylpyridine),[7] and poly(styrene sulfonate).[8,9]

Long before such reports, it was already well known that the viscosity of solutions containing charged particles increases as ionic strength decreases, and that in such solutions containing little or no excess salt, the reduced viscosity increases with decreasing solute concentration.[10] A summary of these effects is contained in a review on the viscosity of linear polyelectrolytes in Ref. 11.

These effects, sometimes referred to as "electroviscous effects," have been the subject of several theoretical treatments, all of which have enjoyed some success when compared to experiment. Some theories have considered the changes in intrinsic viscosity due to the energy dissipation in the polyion–counterion atmosphere, sometimes referred to as the "primary" electroviscous effect.[12–15] The "secondary" electroviscous effect usually refers to viscosity enhancement due to electrostatic interactions between particles. This has likewise been treated theoretically in detail.[8,16–20]

Previous conformationally based explanations, which do not account for all major features of the η_r behavior, however, include those by Fuoss,[6] Witten and Pincus,[21] and Hodgson and Amis.[7] Witten and Pincus, e.g., present an interesting argument for how polyelectrolyte concentration affects persistence length, apart from ionic strength effects, and use this to rationalize the "Fuoss law" for polyelectrolyte reduced viscosity η_r. This latter, however, contains only the monotonic increase of η_r with decreasing Cp, and so the existence of the peak is not addressed.

The purpose here is to propose a conformationally based mechanism to explain the major features of the peak of reduced viscosity vs polyelectrolyte concentration for solutions of long-chain, semiflexible polyelectrolytes at very low ionic strength. No attempt at a rigorous theory is made, but rather demonstrations are made to show the plausibility of the notions and their semiquantitative agreement with experiment and, finally, experiments are proposed which can test the ideas.

Because abundant experimental data show how greatly semi-flexible polyelectrolyte mean square radius of gyration changes with ionic strength, it can be demonstrated that these large dimensional changes lead naturally to the observed viscosity behavior. The primary notion in what follows is that at very low ionic strength it is the two-body interaction term in the total solution viscosity power series expansion, controlled by the particles' effective viscosity volume, which controls the behavior in the peak regime of η_r vs Cp.

It is proposed that this conformationally based model is the limiting case for long, semiflexible polyelectrolytes near the coil limit when $\langle S^2 \rangle^{1/2} \gg \kappa^{-1}$, where $\langle S^2 \rangle$ is the polymer's mean square radius of gyration. At the other extreme, where $\kappa^{-1} \gg \langle S^2 \rangle^{1/2}$ (e.g. for short chains) effects described by previous theories of the electroviscous effect may dominate. κ^{-1} the electrostatic screening length is approximated in what follows as

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$$\kappa^{-1}(\text{Å}) = 97/\sqrt{Cs}(\text{mM}),\tag{1}$$

which is appropriate for aqueous solutions at $T = 25\ ^\circ\text{C}$.

It is important to note that the conformational interpretation presented in this article has sometimes been called the "tertiary" electroviscous effect. It should be pointed out, however, that discussions of the tertiary electroviscous effect have usually been concerned with the increase in solution viscosity due to the increase in the intrinsic viscosity of individual polyelectrolytes as ionic strength decreases. This single-body, intrinsic effect is embodied in the second term on the right-hand side of Eq. (3) below ($\eta_s[\eta]Cp$) and, as discussed below, it is usually negligible compared to the *interaction* term in Eq. (3) ($\eta_s\beta[\eta]^2Cp^2$), which should control the existence and features of the reduced viscosity vs Cp peak.

THE CONFORMATIONAL ORIGIN OF THE VISCOSITY PEAK FOR LONG SEMIFLEXIBLE POLYELECTROLYTES

When one dilutes a polyelectrolyte solution with an aqueous solution of fixed added salt concentration C_a, the dilution process is not isoionic since the osmotically free counterions of the polyelectrolyte itself contribute to the solutions total ionic strength Cs, i.e.,

$$Cs = C_a + \epsilon Cp,\tag{2}$$

where ϵ characterizes the degree of dissociation of the counterions and how they add to the solution's effective ionic strength, and is related to the polyelectrolyte linear charge and mass densities ξ and b/a, respectively. It is to be noted that if "pure water" at $T = 25\ ^\circ\text{C}$ is used for the dilution, C_a will nonetheless be on the order of 10^{-4} mM ($\kappa^{-1} \cong 10^4$ Å) due to the dissociation constant of water, so that it is experimentally impossible to attain $C_a = 0$ under normal conditions. (The large effect of even traces of carbonic acid in solution and the importance of performing experiments under a nitrogen atmosphere was recently demonstrated).[9]

As serial dilution of a polyelectrolyte solution is performed Cs decreases as Cp decreases. The decrease in Cs leads to a continuous expansion of the polyelectrolyte coil at a rate such that the square of the viscometric volume V_v occupied by a given molecule increases more quickly than the mass concentration Cp decreases, leading to a measurable increase in the reduced viscosity of the solution as Cp decreases. This is so since the first interaction term in the expression for viscosity involves the volume fraction squared. As Cp continues to decrease, however, the molecule will begin to approach its maximum size, the viscometric volume of each polymer starts to become independent of Cp and Cs, and so the reduced viscosity goes back down as Cp decreases, and a peak in η_r vs Cp is obtained.

To put this explanation on a quantitative experimental footing, we start with the standard expansion for solution viscosity η, in terms of the viscosity of the pure solvent η_s, the polymer intrinsic viscosity $[\eta]$, and the polymer concentration Cp,

$$\eta = \eta_s + \eta_s[\eta]Cp + \eta_s\beta[\eta]^2Cp^2 + \cdots.\tag{3}$$

β is a complicated function of the two body interactions between polymer chains. In the case of *neutral* polymers, β is found experimentally to be roughly 0.35. No universal value of β for polyelectrolytes is known, although data and tentative theories exist.[22,23]

The reduced viscosity η_r is defined in the standard way as

$$\eta_r = (\eta - \eta_s)/(\eta_s Cp) = [\eta] + \beta[\eta]^2 Cp.\tag{4}$$

The intrinsic viscosity $[\eta]$ is a measure of the hydrodynamic volume of a single polymer. For polyelectrolytes, there is currently no definitive model for $[\eta]$, although considerable progress has been made.[24] A review of such models is not attempted here, but rather we examine the conformational hypothesis in terms of the classical nondraining expression [e.g., Tanford (Ref. 25)]

$$[\eta] = \nu N_A V_v / M,\tag{5}$$

where N_A is Avogadro's number. For an ideal coil polymer approximated by a viscometrically equivalent sphere $\nu = 2.5$ and the viscometric volume is given by

$$V_v = (4\pi/3)\sigma^3\langle S^2\rangle^{3/2},\tag{6}$$

where $\sigma \sim 0.85$ is the proportionality between the root mean square radius of gyration $\langle S^2\rangle^{1/2}$ and the radius of the sphere. In principle, V_v in the nondraining limit is proportional to the cube of $\langle S^2\rangle^{1/2}$, as Eq. (6) indicates. Effects such as draining, excluded volume, interpenetration of polymer coils, and electrostatic enhancement of the interacting volumes, however, are not accounted for in this relationship. A recent work,[26] e.g., proposes a semiempirical proportionality of $[\eta] \propto \langle S^2\rangle^\mu$, where $\mu < 1.5$. Recent work has also shown that hydrodynamic radius R_h is not simply related to $\langle S^2\rangle^{1/2}$ for several linear polyelectrolytes.[27-29] We use Eq. (6) as a concrete starting point, nonetheless. If we assume that V_v is dominated by steric dimensions $\langle S^2\rangle$, and that electrostatic enhancement of V_v due to κ^{-1} is negligible, then Eq. (4) can be written as

$$\eta_r = (4\pi\sigma^3\nu N_A/3M)\langle S^2\rangle^{3/2}$$
$$+ \beta(4\pi\nu N_A\sigma^3/3M)^2\langle S^2\rangle^3 Cp.\tag{7}$$

It has been found experimentally for several long polyelectrolytes near the coil limit (e.g., hyaluronate,[27] polystyrene sulfonate,[28] and partially ionized polyacrylate[29]) that $\langle S^2\rangle$ over the range of about $Cs = 0.001$ to 1 M depends on ionic strength Cs, and polyelectrolyte linear charge density ξ, in the following way:

$$\langle S^2\rangle = (L/3)(L_0' + \xi\gamma/\sqrt{Cs}),\tag{8}$$

where L is the contour length, L_0' is the "apparent intrinsic persistence length" of the polymer, and L_T' the "total apparent persistence length" is given by

$$L_T' = L_0' + \xi\gamma/\sqrt{Cs}.\tag{9}$$

The apparent persistence lengths are amply defined in Refs. 27–29. Both γ, which relates to the change of the polymer's bending and electrostatic excluded volume as Cs varies, and L_0' may sometimes depend on M. Although the origin of such seeming experimental regularity for the dependence of $\langle S^2\rangle$

on ξ and Cs is not fully understood, a qualitative to semi-quantitative understanding of the effect arises when the linearized theories of electrostatic persistence length (EPL) are combined with electrostatic excluded volume (EEV) considerations within the framework of perturbation theory for excluded volume (Refs. 27–35).

Equation (9) is not necessarily expected to hold at extremely low Cs, since the viscosity peak data is usually obtained at values of C_a below those in the corresponding light scattering experiments used to establish Eq. (9); e.g., in the case of HA, the viscosity peak was observed for $C_a \leq 0.2$ mM^2, whereas the range of Eq. (8) found from light scattering was down to about 0.5 mM.[27]

If we consider long molecules near the coil limit and ignore excluded volume effects so that $L = M/(b/a)$, where b/a is mass per unit length of the polymer, then Eq. (7) can be written as

$$\eta_r = (4\pi\nu N_A \sigma^3/3)M^{1/2}[(a/3b)(L_0' + \xi\gamma/\sqrt{Cs})]^{3/2}$$

$$+ (4\pi\nu N_A \sigma^3/3)^2 M[(a/3b)(L_0' + \xi\gamma/\sqrt{Cs})]^3 Cp. \quad (10)$$

It has been found empirically that the perturbed mean square radius of gyration $\langle S^2 \rangle$ can sometimes be related to L_T' via the worm-like chain formula (which normally applies to unperturbed mean square radius of gyration $\langle S^2 \rangle_0$ and true persistence length L_T)[34–37]

$$\langle S^2 \rangle = LL_T'/3 - L_T'^2 + 2L_T'^3/L - 2(L_T'^4/L^2)$$

$$\times [1 - \exp(-L/L_T')]. \quad (11)$$

Figure 1(a) shows computations using Eq. (7) with $\langle S^2 \rangle$ from Eq. (11), where the experimental apparent total persistence length for HA is used[27]

$$L_T'(\text{Å}) = 87 + 307/\sqrt{Cs}(\text{mM}). \quad (12)$$

Additional parameters appropriate to HA are $\epsilon = 1.25$ [from a charge/bjerrum length of 0.7, and Cp in mg/ml in Eq. (2)] and $b/a = 40$ Daltons/Å. M is taken as 1.6×10^6 to approximate HA data in Ref. 2, also shown in Fig. 1(a), and $L = 40\,000$ Å. In the absence of a definitive polyelectrolyte theory of viscosity, β is arbitrarily taken as 1.0 and the net η_r from Eqs. (7), (11), and (12) is scaled by 0.25.

Figure 1(a) shows that the conformational changes of the hyaluronate are sufficient to produce peaks in the behavior of η_r vs Cp, which are qualitatively similar to the experimental data shown. It can likewise be seen that when C_a is ~ 1 mM, the peak no longer exists. For HA of $M = 1.6 \times 10^6$, the number of apparent persistence lengths ranges from roughly 27 to 100 over the range of $Cs = 0.05 - 1$ mM. At the peaks in Fig. 1(a), the contribution of the counterions to the ionic strength, expressed as the ratio of the second to first terms in Eq. (2) ($\epsilon Cp/C_a$), ranges from roughly 2 to 3 as C_a increases.

In Fig. 1(b), computations are made for η_r for the case $C_a = 0.05$ mM based on different considerations for Eqs. (4)–(7). The solid line is the same as in Fig. 1(a), except that η_r is unscaled. The long dashed line shows the computation when the coil limit expressed in Eq. (10) is used and is also unscaled.
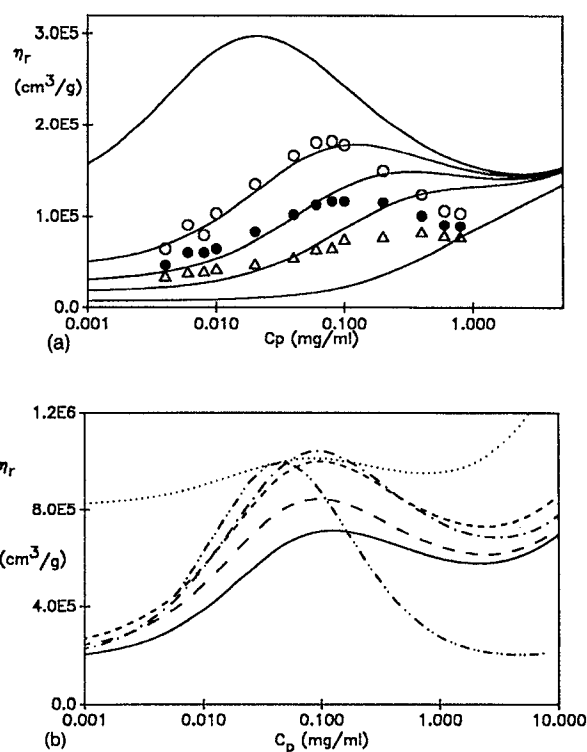

FIG. 1. η_r vs Cp using Eq. (7), with the experimentally determined L_T for HA from Eq. (12) in calculating $\langle S^2 \rangle$ from Eq. (11). $M = 1.6 \times 10^6$, $L = 40\,000$ Å, $\xi = 0.7$, $\epsilon = 1.25$, and $b/a = 40$ Daltons/Å. (Solid lines, from top to bottom) $C_a = 0.01$, 0.05, 0.1, 0.2, and 1.0 mM. Experimental HA results are from Ref. 2 at C_a of $\bigcirc = 0.05$ mM; $\bullet = 0.1$ mM; $\triangle = 0.2$ mM. (b) A comparison of different models and assumptions for Eqs. (5)–(7) for the HA parameters of (a) and $C_a = 0.05$ mM. Each line is described in the text.

The dashed–dotted–dotted line shows the results when $\langle S^2 \rangle$ is calculated via the combined EPL/EEV theories as in Ref. 27, and then used in Eq. (7). The rod diameter d is taken as 10 Å and the curve is scaled by 0.067 to bring its magnitude close to the others. This large overestimate of η_r is consistent with the overprediction of $\langle S^2 \rangle$ at low Cs, characteristic of the EPL/EEV theory, and is discussed below.

The medium dashed line shows the unscaled result of using the Yamakawa Fujii model[37] for $[\eta]$ of worm-like chains with no excluded volume, using Eqs. (40)–(45) from that reference and $d = 10$ Å. The total apparent persistence lengths of Eq. (12) are used instead of the true persistence lengths in Eqs. (40)–(45) as an ad hoc fashion of including excluding volume effects.

The dotted line is using a "Weill–des Cloizeaux relation" of $[\eta] \propto \langle S^2 \rangle^\mu$, where $\mu = 1.25$, $\beta = 10$, and the result is scaled by 100.

The dashed–dotted line shows the result of simply adding κ^{-1} to $\langle S^2 \rangle^{1/2}$ before calculating $[\eta]$ from Eq. (5).

The main result of Figs. 1(a) and (b) is that independent of the model chosen for $[\eta]$, the qualitative behavior of η_r vs Cp for semiflexible polyelectrolytes is predicted. Without a theoretical justification for changing the value of β, or the overall scaling of $[\eta]$, we refrain from generating additional curves or attempting fits to data. Obviously these factors
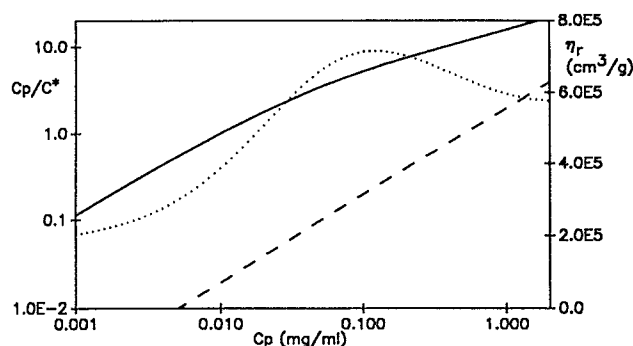
FIG. 2. "Cp/C^*" (not quantitative) of a long, semiflexible polyelectrolyte (solid line) compared to that of an inextensible polymer (dashed line). Parameters are the same HA parameters as in Figs. 1(a) and (b); the solid line uses Eqs. (11) and (12) for $\langle S^2 \rangle$ at $C_a = 0.05$ mM; the dashed line uses a constant dimension $\langle S^2 \rangle = 1080$ Å for HA at very high C_a for computing C^*. The corresponding peaked η_r is shown with the dotted line.

control the relative importance of the two $[\eta]$ terms in Eq. (7), the peak "contrast," width, and other factors, but unless they are set to extreme values, the peak remains.

EFFECTS OF CONFORMATIONAL CHANGE ON THE OVERLAP CONCENTRATION C^*

The magnitude of the second term in Eq. (7) is closely related to the relation between Cp and the "steric overlap concentration" C^*. A very crude estimate of C^* is given by

$$C^*(g/cm^3) \approx M/[(4\pi/3)\langle S^2 \rangle^{3/2} N_A]. \qquad (13)$$

Figure 2 shows a log–log plot of Cp/C^* vs Cp for HA parameters and $C_a = 0.05$ mM. The solid line uses $\langle S^2 \rangle$ from Eqs. (11) and (12) in Eq. (13) (i.e., illustrating the effect of coil expansion on C^*), whereas the dashed line uses the constant value of $\langle S^2 \rangle^{1/2} = 1080$ Å in Eq. (13), which is appropriate for HA at high Cs (i.e., illustrating no coil expansion due to changing Cs). The difference in Cp/C^* with and without coil expansion can run close to two orders of magnitude. The curve of η_r for HA at C_a from Fig. 1(a) is shown as a dotted line.

The absolute ratio Cp/C^* in Fig. 2 should not be taken as quantitative, but rather a guide to how much the expansion effect can increase the value with respect to the neutral polymer (no expansion) case.

FURTHER PREDICTIONS FOR THE REDUCED VISCOSITY BEHAVIOR OF LONG CHAINS

In addition to predicting the existence of the η_r vs Cp peak for low C_a, the conformational explanation predicts (i) the position of the peak for a given C_a; (ii) the position of the peak (Cp) for a given C_a is independent of the polyelectrolyte mass M, (iii) the height of the peak $\eta_{r,p}$ at a given C_a varies as M; and (iv) the height of the peak for a given M varies as roughly $CpCs^{-1.5}$. These features are now examined.

The slope of η_r vs Cp can be investigated from the derivative of Eq. (7)

$$\frac{\partial \eta_r}{\partial Cp} = \left(\frac{\partial \eta_r}{\partial \langle S^2 \rangle} \right) \left(\frac{\partial \langle S^2 \rangle}{\partial L_T'} \right) \left(\frac{\partial L_T'}{\partial Cp} \right)_{\text{terms in } \langle S^2 \rangle}$$

$$+ \left(\frac{\partial \eta_r}{\partial Cp} \right)_{\text{explicit terms in } Cp}. \qquad (14)$$

Carrying this out gives the condition for the peak of η_r vs Cp,

$$\frac{\beta \lambda \langle S^2 \rangle^{5/2}}{M} = \frac{\epsilon \mu}{2(C_a + \epsilon Cp)^{3/2}}$$

$$\times \left[3/2 + \frac{3\beta\lambda}{M} \langle S^2 \rangle^{3/2} Cp \right] \frac{\partial \langle S^2 \rangle}{\partial L_T'}, \qquad (15)$$

where λ is a cluster of constants given by $\lambda = (4\pi\nu\sigma^3 N_A/3)$ and $\mu = \xi\gamma$. If the modified worm-like chain formula (9) is used, then

$$\frac{\partial \langle S^2 \rangle}{\partial L_T'} = L/3 - 2L_T' + 6L_T'^2/L - 8(L_T'^3/L^2)[1 - \exp(-L/L_T')]$$

$$+ (2L_T'^2/L)\exp(-L/L_T'). \qquad (16)$$

While Eqs. (15) and (16) can be programmed on a computer to investigate the existence and properties of the η_r slope and peak, an interesting limiting case is when the second term in Eq. (7) dominates η_r, as it often does at the peak. Then, from Eq. (15),

$$\langle S^2 \rangle = \frac{3\mu\epsilon Cp}{2(C_a + \epsilon Cp)^{3/2}} Cp \frac{\partial \langle S^2 \rangle}{\partial L_T'}. \qquad (17)$$

In the coil limit, this latter equation reduces to

$$L_0' + \mu/(C_a + 1.25\epsilon Cp)^{1/2} = 1.5\mu Cp\epsilon(C_a + \epsilon Cp)^{3/2}. \qquad (18)$$

Under very low ionic strength conditions, where the peak is generally observed, the electrostatic persistence length ($\gamma\xi/\sqrt{Cs}$) is often much larger than L_0' (e.g., for HA at $Cs = 0.1$ mM, $L_e'/L_0 \approx 11$), so that the Cp for the viscosity peak Cp_p at any C_a can be located approximately by

$$Cp_p \approx 2C_a/\epsilon. \qquad (19)$$

This linearity is consistent with reports of the viscosity peak for long molecules. For HA $\epsilon \approx 1.25$, so that $Cp_{\text{peak}} \approx 1.6C_a$. The HA data from Ref. 2 give $Cp_{\text{peak}} \approx 1.8(\pm0.4) \, C_a$.

Under the conditions leading to Eq. (19), the position of the viscosity peak should be independent of the molecular mass of the polyelectrolyte.

According to Eq. (10) (coil limit and ignoring excluded volume effects), the height of the peak of η_r should vary as roughly M, when at the peak, the second (interaction) term is much larger than the leading (intrinsic) term. Figure 5 in Ref. 8 shows that $\eta_{r,p}$ does indeed vary linearly with M for NaPSS over a wide range of C_a values.

When the second term dominates at the viscosity peak, the peak heights for different C_a should scale according to the ratios of the second term in Eq. (10). Under the same conditions leading to Eq. (19), for polymers of a given M at low C_a, the peak viscosity $\eta_{r,p}$ should scale as
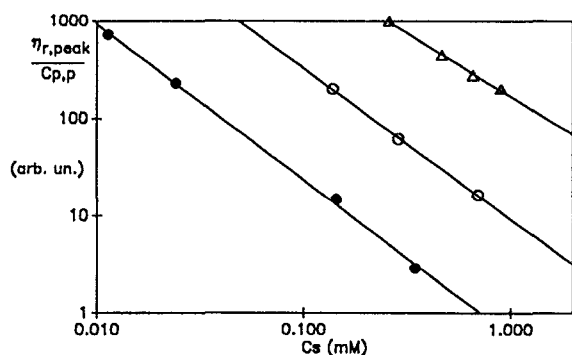
FIG. 3. $\eta_{r,p}/Cp_p$ vs Cs for experimentally determined points for HA (O), NaPSS ($\bullet$ (from Ref. 8)], and polyvinyl sulfate ($\triangle$ from Ref. 13). Slopes (given in the text) are close to -1.5 for each.

$$\frac{\eta_{r,p}}{Cp_p} = C_s^{-1.5}, \qquad (20)$$

where Cp_p is the value of Cp at the peak. Figure 3 shows a log–log plot of η_r/Cp_p vs Cs for HA from Ref. 2, for which the slope is -1.54; for polyvinyl sulfate from Ref. 13 [ϵ is estimated at 0.167 for Cp in mM in Eq. (2)], for which the slope is -1.3; and for data from Fig. 3 in Ref. 8 for NaPSS ($M = 16\,000$, which, however, makes it probably far from the coil limit), for which the slope is -1.6 [$\epsilon = 0.5$, as taken from the relation $Cp/Ca = 4$ in Ref. 8 and Eq. (19) above].

COMMENTS ON ELECTROSTATICALLY ENHANCED EFFECTIVE VOLUME AS A MECHANISM FOR YIELDING PEAKS OF η_r VERSUS CP WHEN $\kappa^{-1} \gg \langle S^2 \rangle^{1/2}$

The principal idea behind Eq. (7) is that the high sensitivity to ionic strength of the dimensions of long polyelectrolytes is in itself sufficient to produce peaks in η_r vs Cp, due to "hard" or steric interactions between polymers, and to account for different aspects of the peaks. There are, however, references to viscosity peak behavior for short chain polyelectrolytes, which may already be close to the polyelectrolyte's maximum expansion over the entire range of C_a, where the peaks are observed (e.g., for $M = 16\,000$ NaPSS in Ref. 8). Hence, while conformational changes of long chain polyelectrolytes are sufficient to cause the experimentally observed peaked viscosity behavior, they may not be necessary for causing viscosity peaks in the case of short chain polyelectrolytes when $\kappa^{-1} \gg \langle S^2 \rangle^{1/2}$. Hence, a different physical mechanism is implied in the latter case.

The theory of electrostatically interacting spheres in Refs. 8 and 16–20 in essence adds an "electrostatically enhanced effective volume" to the basic hard-sphere volume. Such enhanced volumes and the interactions between them have been proposed, e.g., to explain scattering phenomenon from charged particles both theoretically[38,39] and experimentally.[36]

A viscosity theory for particles with interacting electrostatic atmospheres is a highly complex problem, and is approached in some detail in Ref. 16. A grossly oversimplified approach to including the EEV effect with the steric effect, for conceptual purposes only, would be to simply add an
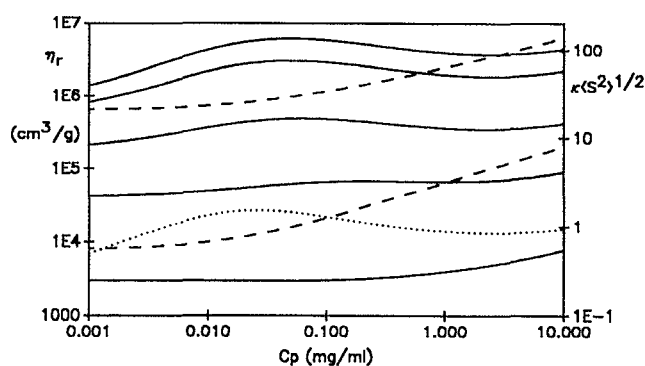

FIG. 4. The effect of M on η_r vs Cp. HA parameters at $C_a = 0.025$ M. (Solid lines from top to bottom) masses of 10^7, 5×10^6, 10^6, 2.5×10^5, and $50\,000$. Dashed lines show $\langle S^2 \rangle^{1/2}/\kappa^{-1}$ (the scale on the right-hand side) for $M = 10^7$ (upper line) and $50\,000$ (lower line). Dotted line adds κ^{-1} to $\langle s^2 \rangle^{1/2}$ for $M = 50\,000$ when computing η_r.

effective electrostatic radius, proportional to κ^{-1}, e.g., to $\langle S^2 \rangle^{1/2}$ in computing V_v in Eq. (5). This indeed enhances the effect and will produce peaks of η_r vs Cp even for short chains. Figure 1(b) includes a curve which adds κ^{-1} to $\langle S^2 \rangle^{1/2}$ to obtain the total $\langle S^2 \rangle^{1/2}$ for use in Eq. (5). Figure 4, mentioned below, includes another such calculation. This heuristic procedure is similar to that proposed by Fuoss.[6]

THE CASE OF SHORT POLYELECTROLYTE CHAINS

As discussed, when $\kappa^{-1} \gg \langle S^2 \rangle^{1/2}$, electrostatically enhanced volumes may dominate as the origin of the peak effect. For "short" chains such as NaPSS of $M = 16\,000$, e.g., the two length scales may be comparable, and there may still be a conformational contribution to the effect [NaPSS end-to-end length is roughly 200 Å and the screening length at $C_a = 0$ and $Cp \sim 10^{-2}$ mg/cm^3, with ϵ 0.9 for Cp in mg/ml in Eq. (2), is ~ 1000 Å].

The combined EPL/EEV model[27–35] predicts that relatively short chains will be very close to the rod limit at these low Cs, so that in principle, there would be little conformational flexibility of the molecules and hence there would be no conformational contribution to the η_r effect. Figure 4 shows η_r vs Cp for HA parameters and different masses, ranging from $50\,000$ to 10^7 according to Eqs. (7), (11), and (12), and how the peak is gradually lost for short chains. The dotted line adds κ^{-1} to $\langle S^2 \rangle^{1/2}$ to compute $[\eta]$ for Eq. (5) and shows that a peak is retained for the lowest mass.

The two dashed lines in Fig. 4 correspond to $\langle S^2 \rangle^{1/2}/\kappa^{-1}$ for the $M = 10^7$ HA case (upper line) and $M = 50\,000$ case (lower line). The scale on the right-hand side shows this ratio to be $\gg 1$ for the high mass, which gives an η_r vs Cp peak, and is on the order of 1 for the low mass, for which no peak occurs when only the steric $\langle S^2 \rangle^{1/2}$ is considered.

Barrat and Joanny[40] have recently assessed the approximations in the Odijk/Fixman/Skolnick (OFS) electrostatic persistence length theory.[31,32] With explicit inclusion of entropic fluctuations in their calculations, they find that at very low ionic strength for semiflexible polyelectrolytes, there should be more flexibility on short length scales than predicted by OFS. Thus, semiflexible polyelectrolytes would not

be expected to approach the rod limit as rapidly as predicted by the OFS theory, so that conformational flexibility may still be available even to short rods at very low Cs.

Meanwhile, there is some experimental evidence that short polyelectrolytes are more flexible than predicted by OSF. Degiorgio et al.[41] found persistence lengths for NaPSS at extremely low Cs much lower than predicted by OSF. Since they used a hydrodynamic model for interpreting the results, however, caution must be used in evaluating this conclusion, since it has been demonstrated that for many polyelectrolytes, hydrodynamic dimensions do not necessarily follow static dimensions as Cs changes.[27–29]

Indirect evidence for chain flexibility at low Cs comes from angular light scattering peaks at extremely low Cp. NaPSS yields angular scattering peaks whose scattering vector at the maximum q_p varies as $Cp^{1/3}$, over a concentration range of $5e-6$ to $5e-5$ g/cm^3 (Refs. 42 and 43). This scaling of q_p has been demonstrated to correspond to the dilute regime for NaPSS as well as for rigid cylinders[44] and DNA.[45] Nonetheless, succinoglycan, (SG) which has a much higher intrinsic rigidity, shows for the same mass, and over the same concentration and scattering vector range and shorter total contour lengths, a scaling of $Cp^{1/2}$, characteristic of scatterers in the semidilute regime.[46] If one applies the EPL/EEV theory to both these polymers at the small equivalent Cs, where these peaks are found, both NaPSS and SG would be predicted to be very close to rod-like, which implies they would be in the semidilute regime at those concentrations. Nevertheless, only SG has the $Cp^{1/2}$ scaling law, but it is already in the semidilute regime by virtue of its high intrinsic stiffness. The fact that NaPSS shows dilute behavior implies it is much more flexible than the rod-like prediction of OSF.

FLEXIBILITY AND SIZE REGIMES, AND PREDICTIONS OF REDUCED VISCOSITY

The equations above can be used to investigate η_r vs Cp behavior for arbitrary polyelectrolyte parameters. The equations for the slope and existence of the η_r peak are not readily decipherable, however, so a specific illustration is given of what "semiflexible" means in the context of peaked η_r behavior. In Fig. 5, the same HA parameters are used as in Figs. 1(a) and (b), except that L_0' the apparent intrinsic persistence length is varied. It is readily seen that as the intrinsic stiffness of these "HA-like" polyelectrolytes increases, the η_r vs Cp curves lose their peak and increasingly resemble those of neutral polymers.

The dotted line shows the effect of adding κ^{-1} to $\langle S^2 \rangle^{1/2}$ for calculating $[\eta]$ from Eq. (5) for the upper curve for which $L_0' = 750$ Å. Such electrostatic enhancement of the polymer size still does not lead to a peak in η_r vs Cp because the molecule is still too rigid and $\langle S^2 \rangle^{1/2}/\kappa^{-1} \gg 1$, and in fact runs from 6.5 to 93 over the Cp range shown. This ratio runs from six to 37 over the same Cp range for the $L_0' = 20$ Å curve, but the conformational changes of this latter molecule are much larger than those of the more rigid one.

There are several more rigid, linear polyelectrolytes for which such viscosity experiments have been performed, and for which η_r is simply a monotonically increasing function
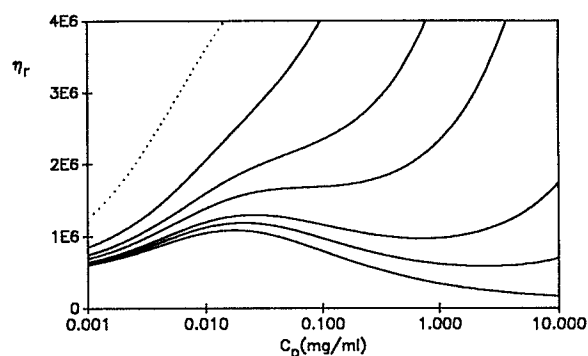

FIG. 5. The effect of intrinsic stiffness on η_r behavior for $C_a = 0.01$ mM; varying L_0' for same HA parameters are the same as in Fig. 1(a) except L_0' varies; (solid lines from top to bottom) $L_0 = 750$, 450, 300, 150, 87, and 20 Å. The dotted line adds κ^{-1} to $\langle S^2 \rangle^{1/2}$ for computing $[\eta]$ via Eq. (5) as explained in the text.

of C_a: DNA (Refs. 47 and 48) (mass not given), xanthan with M around 1 000 000 and $L_0' \sim 300$ Å [Gessler (unpublished results)], and succinoglycan,[46] with $M = 700\,000$ and $L_0' \sim 300$ Å. For xanthan and succinoglycan, in fact, virtually no change in $\langle S^2 \rangle$ was measurable over the range $Cs = 0.001$ to 1 M. For all of these fairly stiff polyelectrolytes $\langle S^2 \rangle \gg \kappa^{-1}$, and it is possible that their rigidity does not allow enough conformational change for the type of η_r effect observed for the more flexible chains of similar mass, as is suggested by Fig. 5.

The contour lengths of the above molecules (except for DNA, mass unknown), including the HA in Fig. 5, are all $\gg 10^4$ Å,) whereas κ^{-1} at a typical $C_a = 0.01$ mM is ~ 1000 Å. Interestingly, the succinoglycan gave a monotonically increasing η_r with Cp, but nonetheless yielded the static and dynamic angular scattering peaks typical of polyelectrolytes.[46]

η_r peaks have nonetheless been reported for certain charged, spherical latex particles with diameters on the order of 1000 Å.[49] These highly symmetric particles have sizes which should be on the order of κ^{-1}, or perhaps even smaller, so that interactions of the electrostatic atmospheres should dominate and η_r behavior qualitatively similar to short chain polyelectrolytes might be expected.

CONCLUSIONS

For long polyelectrolytes, where $\langle S^2 \rangle^{1/2} \gg \kappa^{-1}$, flexible enough that there are still a considerable number of segment lengths at low Cs, there should be peaks in the behavior of η_r vs Cp due almost entirely to the conformational changes that accompany changes in Cs. Using experimentally determined $\langle S^2 \rangle$ and L_T' behavior for HA gives qualitative agreement with this idea. The conformational based explanation also predicts the position of the peak should vary proportionally with Cs and be mass independent in the long chain limit, and the peak height should vary as M for a given C_a, and according to $Cp \times Cs^{-1.5}$ for a given M.

This model predicts that conformational effects will dominate η_r vs Cp behavior via the second term in Eq. (7) as

long as $\kappa^{-1} \ll \langle S^2 \rangle^{1/2}$ and the polyelectrolyte is flexible enough to have sufficient conformational increase as it is diluted. Figure 5 illustrates the meaning of "flexibility" in this context, and Eqs. (15) and (16) allow different polyelectrolyte parameters to be tested. Sufficiently rigid particles in this size limit should show neither a peak in η_r vs Cp nor an increase of η_r with decreasing Cp. Experiments with polyelectrolytes of varying parameters ξ, γ, L, L_0', etc. should show if these predictions are borne out in general.

When $\kappa^{-1} \gg \langle S^2 \rangle^{1/2}$, then the complex interaction of electrostatic atmospheres may dominate over conformational effects and lead to the peak behavior of η_r vs Cp, regardless of whether the particle is flexible or totally rigid. The theories and interpretations of Refs. 8 and 16–20 should apply in this limit.

It is noted that no type of long-range ordering, peculiar anisotropies, domain formation, etc. need be invoked to describe all the major features of the viscosity behavior of long polyelectrolytes at low Cs.

The present work makes plausible a conformational interpretation for the η_r vs Cp behavior of long chain semi-flexible polyelectrolytes at very low ionic strength. Still lacking, however, is a general theory for $[\eta]$, which accounts for electrostatic, draining, and excluded volume effects, and for β, which deals with the hydrodynamics of single contact interactions between polyelectrolyte chains.

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