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Viscosity of Weakly Charged Polyelectrolyte Solutions: The Mode-Mode Coupling Approach[§]

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ABSTRACT: A model based on mode-mode coupling approximation (MMCA) to describe the reduced viscosity η_r of weakly charged polyelectrolyte solutions is proposed. The variation of η_r with the polyelectrolyte concentration C_p exhibits a peak. The effects of charge parameter f, added salt concentration C_s, and molecular weight M_w are presented with and without hydrodynamic interactions, corresponding respectively to the Zimm and Rouse models. Both models give the same features but are quantitatively different.

I. Introduction

Polyelectrolyte solutions differ considerably from neutral polymers with respect to their scattering properties and viscosity behaviors. Indeed, flexible polyelectrolyte solutions, in the absence of added salt, present a peculiar behavior with respect to their viscosity data: Above a certain concentration (in semidilute and concentrated domains) denoted C_{pmax}, the reduced viscosity $\eta_r = (\eta - \eta_0)/\eta_0 C_p$, where η_0 is the solvent viscosity, increases when the polyelectrolyte concentration C_p decreases. This abnormal concentration dependence, in contrast to ordinary polymer solution behavior, is described by the empirical Fuoss law:[1]

$$\eta_r = \frac{A}{1 + BC_p^{1/2}} \tag{1}$$

This equation summarizes quite well the behavior of η_r in the semidilute regime although it has no fundamental theoretical basis and fails to describe the molecular weight and the charge effects on the viscosity. These parameters do not appear explicitly in this relation.

Recently, there were attempts[2,3] to develop theoretical bases for the Fuoss law. The first one is due to Witten and Pincus[2] who used a model suitable for a highly charged polyelectrolyte assuming that the persistence length L_p is essentially due to electrostatic effects: This L_p is comparable to the Odijk[4] electrostatic persistence length L_e in the dilute system. From energy balance arguments, they made predictions not only on the concentration behavior but they were able also to obtain the scaling laws of the constants A and B in terms of molecular weight M_w and charge Z of the polymer:

$$A/B \approx Z^2 b^{3/2} \propto M_w^2 \tag{2a}$$

$$A \approx (bZ)^3 \propto M_w^3 \tag{2b}$$

where $b = (\lambda_B r^2)^{1/2}$, $\lambda_B = e^2/\epsilon kT$ is the Bjerrum length, and r is the end-to-end distance between charged segments.

The second model was proposed by Rabin[3] and uses a phenomenological relationship between the viscosity, the shear modulus E, and the stress relaxation time τ. The results show that the reduced viscosity scales as $C_p^{-1/2}$ (the Fuoss law) with

$$A/B \approx Z \propto M_w \tag{3}$$

but no relationship for the constant A is given.

The experimental results of Kim and Peiffer[5] have been found to support Rabin's model, i.e. $A/B \approx M_w$. Moreover, Strauss et al.[6] showed, by extrapolating the experimental results to $C_p \to 0$, that A varies approximately as M_w^2. These results are different from the predictions of Witten and Pincus, eq 2. More recently, results obtained on a fully charged polyelectrolyte (sodium polystyrenesulfonate: NaPSS) were reported by Cohen, Priel, and Rabin.[7] The model they have used to interpret the experimental results captures the qualitative features of the experimental data, namely (i) the existence of a maximum of the reduced viscosity η_r versus C_p and (ii) the height of the maximum is linearly proportional to the molecular weight of the polyion and decreases with salt concentration.

This model was based on the mode-mode coupling approximation (MMCA) of Hess and Klein,[8] and although it seems to fit quite well the experimental data,[7] there are several features in their application of this theory which are not clear and need further specifications. The form of the structure factor $S(q)$ and in particular the form of the direct correlation function $C(q)$ are not suitable for linear polymers, they are good only for point charges. The form-factor $P(q)$ of the polymer does not appear explicitly which means that it was assumed to be equal to 1. Moreover, an approximation for the direct correlation function and its derivative have been used, and they obtained the following result

$$(\eta - \eta_0)/\eta_0 \approx C_p^2/\kappa^3 \tag{4a}$$

which is the original formula of Hess and Klein[8] for charged point-particles and reproduces the concentration behavior of the Fuoss law for C_p higher than the overlap concentration C^* since

$$\kappa^3 \approx C_p^{3/2} \tag{4b}$$

here $\kappa^2 = 4\pi\lambda_B(f\varphi_p + \Phi_s)$ is the square of the inverse Debye screening length, where f is the charge parameter (the fraction of charged monomers within a polyion), Φ_p and Φ_s are the polyelectrolyte and added salt concentrations, respectively [Φ_p represents the concentration in number of monomers per unit volume; its relation with C_p, expressed in g/cm³, is simply $C_p = m_0\Phi_p/N_{av}$, where m_0 is the molecular weight per monomer and N_{av} is Avogadro's number], and $\lambda_B = (e^2/\epsilon k_B T)$ is the Bjerrum length, where ϵ is the dielectric constant of the solvent, e.g. $\lambda_B \approx 7$ Å in

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water. This treatment, when applied to polyelectrolyte solutions, seems to us inconsistent and uncontrollable. In the present model, we use the full expression of the structure factor $S(q)$ derived by Joanny and Leibler,[10a] using a free energy model with fluctuations, and independently by us,[10b] using the Edwards Hamiltonian formalism. We restrict ourselves to weakly charged polyelectrolyte solutions, and the results obtained here can be extrapolated to strongly charged polyelectrolytes as we will show in a forthcoming paper. Furthermore, the hydrodynamic interaction was completely neglected in the model of Cohen, Priel, and Rabin,[7] and one knows that this type of interaction is important for solutions and especially in the dilute range. We think that these effects should be included in the description of the reduced viscosity of linear polyelectrolyte, and this is one of the goals of the present paper. The inclusion of such interactions shows that the values of the viscosity are substantially modified.

II. Theory

As pointed out earlier in this paper, we apply a model originally developed by Hess and Klein[8] and based on the MMCA[11,12] to weakly charged polyelectrolyte solutions. This approximation leads to a nonlinear self-consistent formulation of interacting Brownian particles. It has been successful in the study of critical phenomena,[12,13] dynamical properties of simple liquids,[14] and localization transition in a Lorentz gas.[15] Using the MMCA, Hess and Klein obtained the following expression for the time-dependent shear viscosity:[8]

$$\eta_s(t) = \frac{k_BT}{2}\frac{{\Phi_p}^2}{(2\pi)^3}\int_0^\infty d^3q\, I^2(q,t)\left\{\frac{q}{I^2(q)}\right\}^2\left[\frac{\partial H(q)}{\partial q}\right]^2 \quad (5)$$

where q, t, and k_BT are the momentum transfer, the time, and the thermal energy, respectively. The reduced viscosity can be obtained from eq 5 using the following relationship:

$$\eta - \eta_0 = \int_0^\infty \eta_s(t)\,\mathrm{d}t \quad (6)$$

In eq 5, the total two-particle correlation function $H(q)$ is defined via the structure factor $S(q)$ as $S(q) = 1 + \Phi_pH(q)$. $I(q)$, $S(q)$, and $I(q,t)$ are given by eqs 9, 10, and 12, respectively. In this paper, as we have mentioned earlier, we restrict ourselves to weakly charged polyelectrolyte solutions. This is the case where only a fraction f of monomers within a chain carries charges. The total amount of charges per chain is given by $Q = efN$, and the electrostatic energy is

$$E_{el} \approx \frac{e^2f^2N^2}{\epsilon k_BTR} \quad (7)$$

which has to be compared to the entropy of the chain $\approx R^2/Nl^2$. R and N are the size and the degree of polymerization of the chain. The use of the Ginzburg criterion shows that (see Joanny and Leibler)[10a]

$$f \le (l/\lambda_B)N^{-3/4} = f_{min} \quad (8)$$

If $f \le N^{-3/4}$, we expect no significant effect of the charges so that we extrapolate our results to the case where $f \ge f_{min}$ but still less than 1 ($f \ll 1$). We will come back to this point in the discussion. In the case of weakly charged polyelectrolyte solutions, which is of interest in the present work, the scattering intensity $I(q)$ has been calculated recently[9,10] on the basis of the Edwards Hamiltonian formalism in RPA approximation and is given by

$$I(q) = \Phi_pNP(q)S(q) \quad (9)$$

with

$$S(q) = \frac{1}{1 + \Phi_pNP(q)[v + \alpha(q)]} \quad (10)$$

where $P(q)$ is the form factor, see eq 17 and v and $\alpha(q)$ are the neutral and the electrostatic contributions to the total excluded volume parameter. $\alpha(q)$ is the Fourier transform of the potential of mean force between monomers assumed to be of the Debye–Hückel form: The monomers are assumed to be point-charges, and their finite size is introduced through their finite excluded volume parameter. In the analysis done by Genz et al.,[9b,c] the monomers are assumed to have finite sizes in both their electrostatic and thermodynamic interactions.

$$\alpha(q) = \frac{4\pi f^2\lambda_B}{q^2 + \kappa^2} \quad (11)$$

We shall assume that the dynamic scattering intensity $I(q,t)$ is a simple exponential decay function:

$$I(q,t) = I(q)e^{-\Gamma(q)t} \quad (12)$$

where $\Gamma(q)$ is the first cumulant[16,17] or characteristic decay frequency. This form of $I(q,t)$ is an approximation since eq 6 involves an integral over all t. We have also neglected the memory effects which may be important in certain cases at long times. A more realistic model should include these effects but this is beyond the scope of this work.

The aim of this work is to investigate the variation of the reduced viscosity

$$\eta_r = \frac{(\eta - \eta_0)}{\eta_0C_p} = \frac{1}{\eta_0C_p}\int_0^\infty \eta_s(t)\,\mathrm{d}t \quad (13)$$

as a function of the polyelectrolyte concentration (Φ_p: volume fraction or C_p in g/cm^3) for various cases. We are mainly interested in the effect of added salt C_s, charge parameter f, and molecular weight M_w. A detailed analysis of the effects of these quantities has been made in the Rouse limit, neglecting the hydrodynamic interactions. These interactions have been introduced in one particular example to show the modifications due to the hydrodynamic back-flow.

A. Rouse Model. In general the first cumulant is given by[16,17]

$$\Gamma(q) = q^2k_BT\frac{M(q)}{\Phi_pNP(q)S(q)} \quad (14)$$

where $M(q)$ is the generalized mobility. In the absence of hydrodynamic interactions $M(q)$ is q-independent and is given by $M(q) = M_0 = \Phi_p/\zeta$ where ζ is the friction coefficient per monomer and therefore eq 14 becomes:

$$\Gamma(q) = q^2k_BT\frac{1}{\zeta NP(q)S(q)} \quad (15)$$

After a straightforward manipulation, one obtains

$$(\eta - \eta_0) = \frac{N\zeta}{8\pi^2}\int_0^\infty \mathrm{d}q\, q^2\frac{P(q)}{S(q)}\left[\frac{\partial S(q)}{\partial q}\right]^2 \quad (16)$$

An analytical expression of the viscosity is difficult to obtain because of the complexity of this integral. For this reason, we have performed numerical calculations in order to illustrate the expected behavior of the reduced viscosity with the polymer concentration in various cases. It is convenient to use a well-known standard experimental notation and write $\upsilon\Phi N = 2A_2M_wC_p$, where A_2 is the second virial coefficient and C_p is the polyelectrolyte concentration in g/cm^3. Since only weakly charged polymers are considered ($f \ll 1$), we assume that the chains are flexible enough to satisfy Gaussian statistics. This allows us to write for the form factor the following expression:

$$P(q) = \frac{2}{u^2}(e^{-u} + u - 1) \qquad (17)$$

where $u = (qR_g)^2$, $R_g{}^2 = Na^2/6$ is the square of the radius of gyration, a being the Kuhn statistical length. As a first-order approximation we have deliberately made R_g constant (it depends only on the degree of polymerization N). In fact R_g has been calculated by Vilgis and Borsali[10b] and the result shows that R_g is a complicated function of N, C_p, C_s, A_2, and f. This choice of $P(q)$ and R_g has some implications on the properties of η_r but is by no means a limitation of our model. One can certainly use a more realistic model depending on the conditions desired as long as the weak electrostatic effects requirement is satisfied.

(i) Effect of Salt. In Figure 1a, we have plotted the variation of the reduced viscosity η_r as a function of log $[C_p]$ for different values of added salt concentrations (C_s = 0.2 × 10^{-5}, 0.4 × 10^{-5}, 0.5 × 10^{-5}, 0.7 × 10^{-5}, 10^{-5}, and 2 × 10^{-5} mol/cm^3), choosing f = 0.1, M_w = 10^6, A_2 = 10^{-4} cm^3/g^2, and $a = \lambda_B \approx 7$ Å. The maximum polymer concentration in this plot is about 5C^* (where C^* is the overlap concentration). All the curves exhibit a maximum. The positions and heights of the maxima depend significantly on the value of added salt concentration C_s. One observes that adding salt moves the maxima toward higher C_p and lowers the value of the reduced viscosity. Furthermore, the position of the peak C_{pmax} increases linearly with the concentration of added salt C_s. This is shown in Figure 1b where we have plotted C_{pmax} versus C_s. The fact that C_{pmax} increases with C_s is expected. Indeed, adding salt to the system enhances the neutral polymer behavior by reducing progressively the effects of electrostatic interactions. The same effect is observed on fully and weakly charged polyelectrolyte solutions[7,18-22] with in fact different slopes of C_{pmax} versus C_s. Indeed, as we will show later, the slope depends on the charge parameter f and the molecular weight M_w. However, for a strongly charged polyelectrolyte the use of the Debye function, eq 17, is doubtful and it has to be replaced by a more adequate form. This is in general a yet unsolved problem, and we refer the reader to a forthcoming paper where this matter is discussed in more detail.

(ii) Effects of Charges. With regard to the effect of charge parameter f (we recall that f is the fraction of charged monomers within the chain), we have plotted in Figure 2a the reduced viscosity as a function of log $[C_p]$ for several values of f, namely f = 0.06, 0.08, 0.1, 0.15, and 0.2, at one salt concentration C_s = 10^{-5} mol/cm^3. One observes that the increase of f moves the maximum toward lower C_p and at the same time increases the value of the reduced viscosity. To understand this behavior, one can invoke the same argument as in the case of added salt, namely that the polyelectrolyte effect is enhanced when f increases. These two behaviors (salt and charge parameter effects) show clearly the balance of these two effects on the screening of electrostatic interactions: decreasing f is equivalent to increasing the salt concentration but in a slightly different way. One may try to fit the variation of C_{pmax} with f by a scaling function of the type $C_{pmax} \approx f^{-x}$. The result gives $x \approx 2$, as shown in Figure 2b. Note that this is significantly different from Cohen et al. result who predicted a variation of the type $C_{pmax} \approx f^{-1}C_s$ (see eq 4). This result can be checked experimentally.

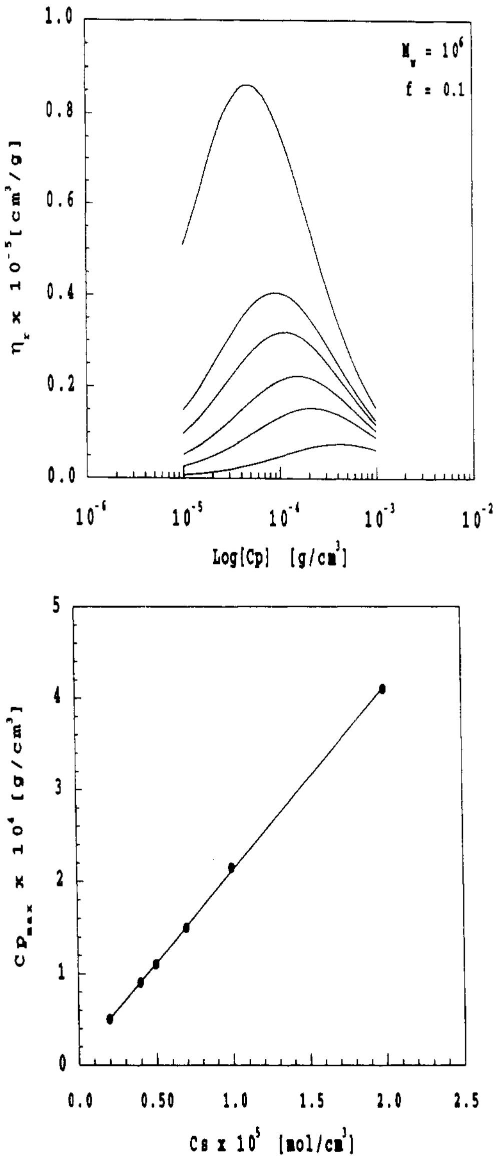

Figure 1. Effect of salt. (a) Variation of the reduced viscosity $\eta_r = (\eta - \eta_0)/\eta_0C_p$ as a function of log $[C_p]$ for f = 0.1, M_w = 10^6, A_2 = 10^{-4} cm^3/g^2, $a = \lambda_B$ = 7 Å, and several values of the salt concentration: (from top to bottom) C_s = 0.2, 0.4, 0.5, 0.7, 1, and 2 (all ×10^{-5} mol/cm^3). (b) Variation of C_{pmax} (concentration at the maximum of η_r) as a function of added salt concentration C_s for the same parameters as in Figure 1a. This figure shows the linear increase of C_{pmax} with C_s.

(iii) Effect of Molecular Weight. The variation of the reduced viscosity with log $[C_p]$ is plotted on Figure 3a for C_s = 10^{-5} mol/cm^3 and f = 0.1 at different molecular weights M_w (M_w = 10^6, 0.6 × 10^6, and 0.4 × 10^6). One observes that the peaks are M_w-dependent. An increase in molecular weight shifts the position of the peak to lower C_p and increases the value of the reduced viscosity. This behavior is expected since when the molecular weight increases, the chain carries a larger number of charges and the polyelectrolyte behavior is recovered at lower C_p with a higher strength. In Figure 3b the values of C_{pmax} as a function of M_w are reported and the fit shows that C_{pmax} scales with M_w as $C_{pmax} \approx M_w{}^{-y}$, where y = 1. In the case of fully charged polyelectrolyte solutions the position of the maximum seems to be independent of M_w at low temperatures[7] and increases with M_w as the temperature increases.[21] For weakly charged polyelectrolytes, we expect

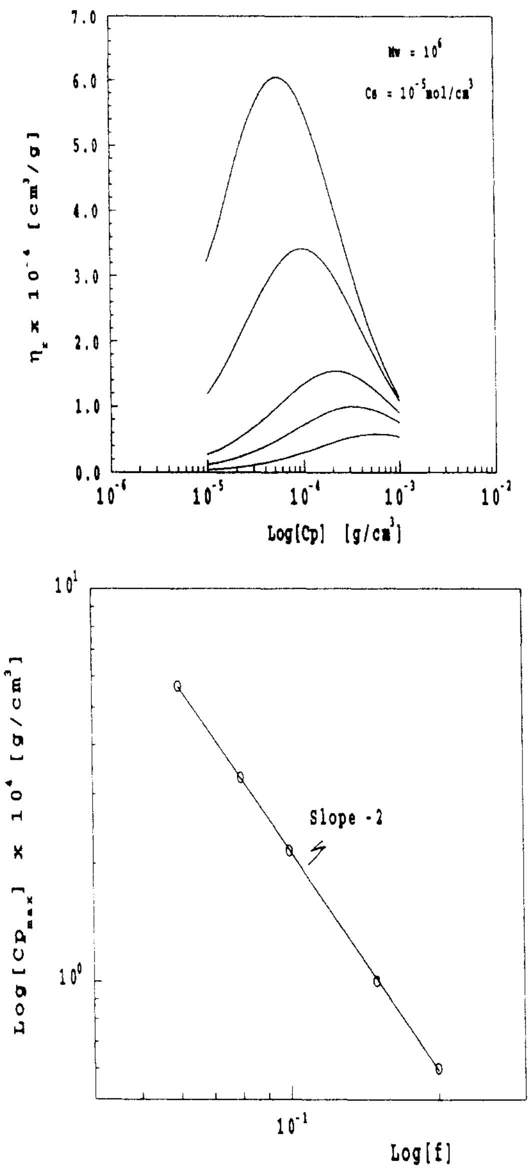

Figure 2. Effect of charge parameter. (a) Variation of η_r as a function of log $[C_p]$ at $C_s = 10^{-5}$ mol/cm^3 for different charge parameters f: (from top to bottom) f = 0.2, 0.15, 0.10, 0.08, and 0.06. The other parameters are the same as in Figure 1. (b) Variation in log–log plot of C_{pmax} as a function of f. This figure shows that C_{pmax} scales with the charge parameter as f^{-2}.

that the position of the maximum changes with the molecular weight.

B. Effects of Hydrodynamic Interactions. In the last section, we presented the behavior of the reduced viscosity as a function of the polyelectrolyte concentration for various values of the charge parameter, the salt concentration, and the molecular weight. The investigation was based on the Rouse limit since the hydrodynamic interactions were neglected. If one takes into account these interactions, the mobility $M(q)$ becomes q-dependent and using the Oseen-tensor description,[16] one obtains

$$\eta - \eta_0 = \frac{N\zeta}{8\pi^2}\int_0^\infty \mathrm{d}q\, q^2\frac{P(q)}{S(q)}\left[\frac{\partial S(q)}{\partial q}\right]^2\frac{1}{1+\mathcal{H}(q)} \qquad (18)$$

where $\mathcal{H}(q)$ is the hydrodynamic term given by

$$\mathcal{H}(q) = \left(\frac{3}{4\pi}\right)aN\int_0^\infty \mathrm{d}k\left(\frac{k}{q}\right)^2 P(k)S(k)\times \left\{\frac{q^2+k^2}{2qk}\log\left|\frac{k+q}{k-q}\right| - 1\right\} \qquad (19)$$

In this relation, the monomer friction coefficient ζ is given by the Stokes–Einstein relation $\zeta = 3\pi\eta_0 a$, where a is the monomer diameter. This is our central result and one notes that it reduces to eq 16 when the hydrodynamic interactions are neglected [i.e. $\mathcal{H}(q) = 0$]. In order to illustrate the effect of these interactions on the reduced viscosity, we have plotted in Figure 4 the variation of η_r as a function of log $[C_p]$ for $C_s = 10^{-5}$ mol/cm^3, $f = 0.1$ and $M_w = 10^6$. Curves a and b represent the Rouse and the Zimm chain models, respectively. One observes that the hydrodynamic interactions do not change the qualitative behavior of the viscosity but its value is dramatically reduced by almost 2 orders of magnitude for the parameters chosen in these calculations.

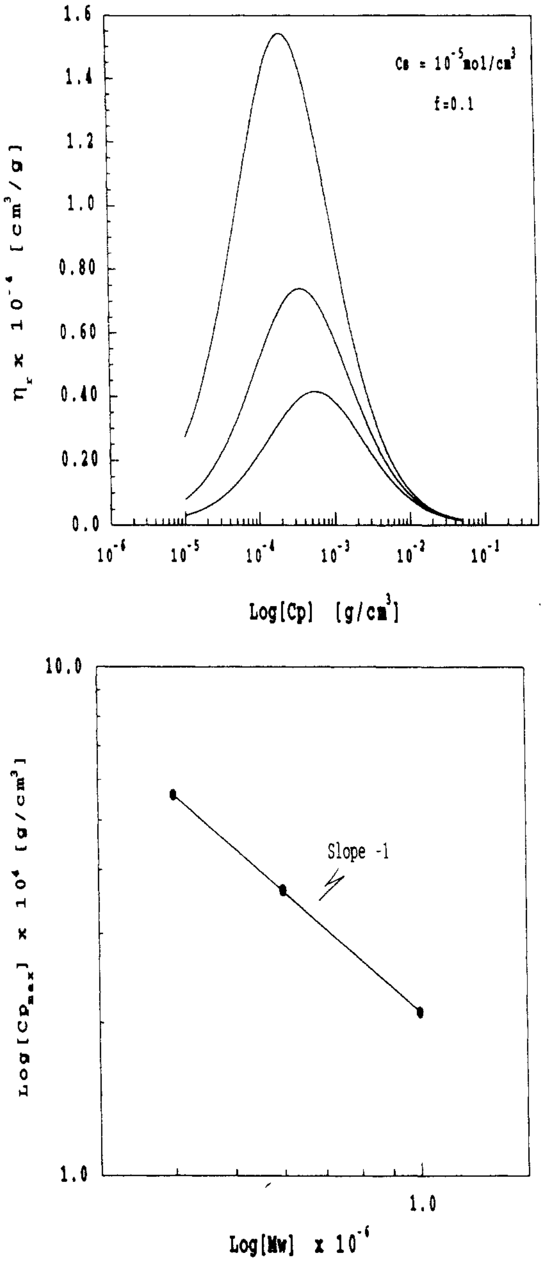

Figure 3. Effect of molecular weight. (a) Variation of η_r as function of log $[C_p]$ for $f = 0.1$, $C_s = 10^{-5}$ mol/cm^3, and three values of the molecular weight: (from top to bottom) $M_w = 10^6$, 0.6×10^6, and 0.4×10^6. (b) Variation in log–log plot of C_{pmax} as function of M_w. This curve shows that C_{pmax} varies with the molecular weight as M_w^{-1}.

III. Conclusions

We have presented in this paper a model based on mode–mode coupling approximation which describes the reduced viscosity behavior η_r for weakly charged polyelectrolyte-

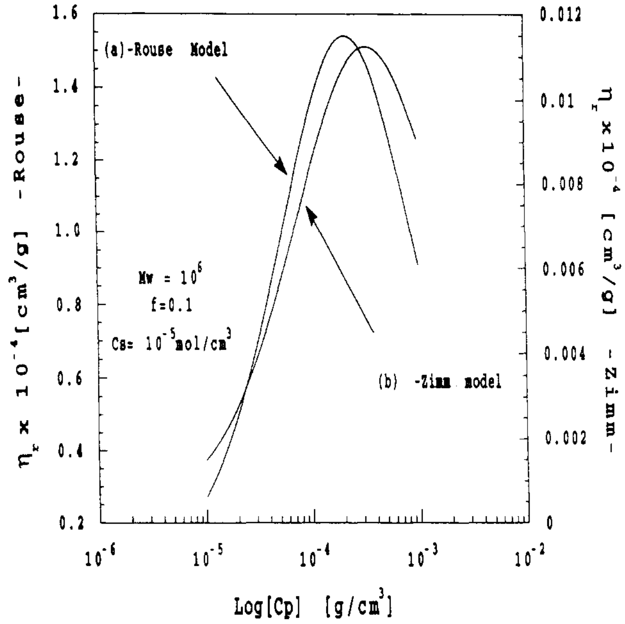

Figure 4. Effect of hydrodynamic interactions. Variation of η_r as a function of log $[C_p]$ at $C_s = 10^{-5}$ mol/cm^3, $f = 0.1$, and $M_w = 10^6$. Curve a corresponds to the Rouse model and curve b shows the effect of the hydrodynamic interactions.

solutions. The results of these calculations show the existence of a maximum in η_r at a certain polyelectrolyte concentration C_{pmax}. The variation of η_r as a function of C_p for various salt concentrations C_s, the charge parameter f, and molecular weight M_w gives the following results: (i) Adding salt to the system decreases the reduced viscosity and moves the position of the maximum toward higher C_p. The numerical calculation show that $C_{\mathrm{pmax}} \sim C_s$. We expect a change in the slope depending on the charge parameter. (ii) Increasing the fraction of charged monomer within the polyion, f, enhances the polyelectrolyte effect by shifting C_{pmax} to lower values such as $C_{\mathrm{pmax}} \sim f^{-x}$ with $x \approx 2$. (iii) For the molecular weight dependency, we found that $C_{\mathrm{pmax}} \sim M_w^{-y}$ with $y \approx 1$. This result is quite different from that reported experimentally for fully charged polyelectrolyte solutions.[7,21]

We would like to go back to the point of using the Debye function for $(1/N^{3/4}) < f \ll 1$. This is in principle inconsistent, but we are confident that our results can be extrapolated to this regime. To be more precise, this theory can be extended self-consistently. The simplest model relies on a scaling argument: i.e. if we let f constant such as $f \sim N^{-3/4+\mu}$, we find immediately for the single chain that $R \sim N^{\nu}$ with $\nu = {}^1/_2 + (2/3)\mu$, where μ is given by the value of f and N. Therefore the bare structure factor would be

$$S(q) = \frac{NC_p}{1 + (ql)^{1/\nu}}$$

Note that $0 < \mu < {}^3/_4$ extrapolates between $\nu = {}^1/_2$ for a Gaussian and $\nu = 1$ for a fully extended chain. This scaling argument is completely ad hoc and has to be seen as a crude approximation to the real effect. It is, of course, only heuristic, but it may help to analyze the data for charged polymers with $f > N^{-3/4}$.

Another more precise way to obtain $S(q)$ is to use a wormlike chain model in its simplest version. The Hamiltonian of the chain consists of the standard Wiener measure and the stiffness term $\beta\epsilon\int_0^N\{\partial^2R/\partial n^2\}^2$. The bending energy $\beta\epsilon$ can be estimated by balancing the stiffness term and the electrostatic energy leading to a very strong benbing energy $\beta\epsilon \sim f^2N^{3/2}$. Thus if $f \sim 0(N^{-3/2})$, $\beta\epsilon$ is negligible but when $f \sim N^{-3/4+\mu}$ we find $\beta\epsilon \sim N^{2\mu}$. Thus we may replace $P(q)$ by the appropriate function for the wormlike chain, but we expect no significant changes of the principal results given in this paper. Such a function has been proposed, for instance, by des Cloiseaux and Jannink.[23] A more relyable calculation has been done by Qian and Kholodenko.[24] They applied a variational calculation to express the rigidity Σ as a function of the charge parameter f (via κ). Thus a polyelectrolyte chain becomes semirigid with an effective bending energy of $\mathrm{E}(\kappa)$; i.e. its Hamiltonian is given by

$$H = \frac{1}{2}\epsilon\int\left\{\frac{\partial u}{\partial s}\right\}^2 + \frac{3}{2l}\int u^2(s)\,\partial s$$

where $u = \partial R/\partial s$ (a constraint $u^2(s) = 1$ has to be employed). The scattering function of such a chain can be calculated (see ref 23). A very elegant calculation of $S(q)$ of the semirigid chain can be found in ref 25.

This formalism can be also applied to more complex systems involving polymer mixtures with or without electrostatic and/or hydrodynamic interactions.

Finally, experimental studies on weakly charged polyelectrolyte solutions are under investigations in order to test these theoretical predictions.

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