Polyelectrolyte Charge Effects on Solution Viscosity of Poly(acrylic acid)

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A scaling theory for polyelectrolyte solution viscosity[1] was recently tested for its predictions of the dependence of viscosity η on polyelectrolyte concentration c and salt concentration c_s, using the sodium salt of sulfonated polystyrene[2] (NaPSS). These experiments confirmed several important predictions of the scaling theory. The semidilute unentangled regime covers a broad range of concentration for high molecular weight polyelectrolytes with no added salt. The relaxation time τ is a decreasing function of concentration in this regime. Despite its qualitative successes, the theory does not seem to predict quite the right exponents for viscosity ($\eta \sim c^{0.35}$ instead of the predicted $\eta \sim c^{1/2}$) and relaxation time ($\tau \sim c^{-0.9}$ instead of $\tau \sim c^{-1/2}$). Furthermore, the scaling theory also makes predictions about the dependence of viscosity on the effective charge of the polyelectrolyte chain in solution, which cannot be tested using NaPSS because the sulfonic acid is too strong. Here we test the predicted dependence of viscosity on effective polyelectrolyte charge and salt concentration, using a weak acid polyion, poly(acrylic acid), neutralized to various extents with NaOH.

We obtained poly(acrylic acid) as a 25% solution in water from Polysciences. The manufacturer's reported molecular weight of 90 000 is reasonably close to the number-average molecular weight $M_n = 128\,000$ (pullulan equivalent) measured by SEC in aqueous 0.1 M sodium acetate containing 25% methanol by volume. The SEC indicates that the sample has a quite broad distribution of chain lengths, with $M_w/M_n > 6$. We exhaustively dialyzed this polymer by flushing many liters of distilled deionized water through the sample and a 20 000 molecular weight cutoff Amicon dialysis membrane. A large $c = 10$ mM (0.01 mol of acrylic acid monomer per liter) stock solution was prepared, from which all solutions were made (this concentration was checked by titration with NaOH). Solutions (300 mL) were titrated with the desired equivalents of NaOH and transferred to the rheometer after thorough stirring. The fraction f of effectively charged monomers was determined by measuring the activity of Na^+ ions in solution using a sodium-selective electrode (Orion). This electrode was calibrated using NaBr solutions, for which a plot of EMF vs ln c_s is a straight line (Nernst equation). We assume that the EMF of a poly(acrylic acid) solution indicates the concentration of free (dissociated) Na^+ ions in solution.

A Rheometrics Stress Rheometer RSR-8600 was modified with an acrylic concentric cylinder geometry.[3] This controlled stress rheometer applies torque using a drag cup motor attached to a rotor that has an air bearing. The inner cylinder of our rheometer cell, with a length of 3.5 in. and a diameter of 4.5 in., is attached to this rotor. This inner cylinder is filled with water as needed for maintaining neutral buoyancy. The outer cylinder is 4.75 in. in diameter, and has a circulating temperature-controlled water bath on its exterior. The viscometer was calibrated with water and several low viscosity standard fluids. The applied stress was varied in the range 0.03 to 0.3 dyn/cm^2 to ensure that the reported viscosities correspond to the zero shear rate limit.

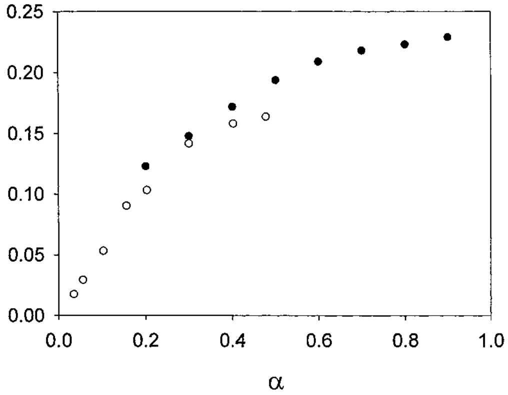

Figure 1. Fraction of monomers bearing an effective charge as a function of neutralization extent. Filled circles are data from this work, determined by a sodium-selective electrode. Open circles are determined from the osmotic pressure data on poly(acrylic acid) gels by Weill et al.[8]

For each neutralization extent, the viscosity of the solution with no added salt was measured first, and then NaBr was progressively added and mixed in the rheometer, to make salt concentrations of 0.5 mM < c_s < 8 mM. Thus, we studied polyelectrolyte solutions in the crossover regime between the low salt limit where there are many more free counterions than salt ions ($fc \gg 2c_s$) and the high salt limit ($fc \ll 2c_s$). The scaling theory[1] describes the specific viscosity η_{sp} of unentangled semidilute polyelectrolyte solutions, in a good solvent for the uncharged monomer, with a simple crossover function.

$$\eta_{sp} \equiv \frac{\eta - \eta_s}{\eta_s} \cong N(cb^3)^{1/2}\left(\frac{f^2 l_B}{b}\right)^{3/7}\left(1 + \frac{2c_s}{fc}\right)^{-3/4} \quad (1)$$

N is the degree of polymerization, c is the monomer number density, b is the monomer size, and l_B is the Bjerrum length where the Coulomb energy between two charges is equal to the thermal energy ($l_B = e^2/(\epsilon kT) =$ 7 Å in water, where ϵ is the dielectric constant, k is Boltzmann's constant and T is the temperature). In this study the only variables are the fraction f of effectively charged monomers and the salt concentration c_s.

The fraction of effectively charged monomers was varied by titration of the polymer with NaOH. The neutralization extent α is defined as the molar equivalents of NaOH added per acrylic acid monomer. α is, therefore, the fraction of acid groups along the chain that have been converted to sodium salts. Since some Na^+ counterions may condense on the chain,[4−7] we need a separate measure of the fraction f of effectively charged monomers. In Figure 1, we plot f as a function of α. The filled symbols are our data, determined with a sodium-selective electrode. The open symbols are calculated from the data of Weill et al. on osmotic

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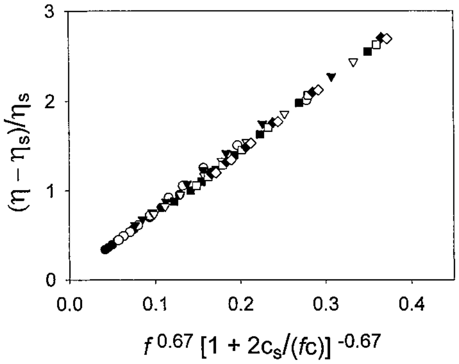

Figure 2. Specific viscosity reduced by the scaling form with empirical exponents. Filled circles have $\alpha = 0.2$; open circles have $\alpha = 0.3$; filled triangles have $\alpha = 0.4$; open triangles have $\alpha = 0.5$; filled squares have $\alpha = 0.6$; open squares have $\alpha = 0.7$; filled diamonds have $\alpha = 0.8$; open diamonds have $\alpha = 0.9$.

pressure of partially neutralized poly(acrylic acid) gels,[8] as $f = \pi/(ckT)$, where π is the osmotic pressure.[1,9] We intentionally keep $\alpha \geq 0.2$ so that we can safely ignore dissociated acid groups on the chain.[10] The agreement between the two very different measures of f is remarkable (within the experimental error which we estimate to be ±10% for both methods). The fraction of effectively charged monomers qualitatively agrees with the Manning–Oosawa expectation of a linear increase at low α, with a saturation at high α that is consistent with counterion condensation keeping the distance between effective charges no smaller than the Bjerrum length.[5,6] However, the experimental crossover between these two limiting behaviors is quite broad, as has also been observed recently from the osmotic pressure of partially sulfonated polystyrene.[11]

The dependence of viscosity on the fraction of effectively charged monomers with no added salt was found to obey a power law.

$$\eta \sim f^{m} \quad \text{with} \quad m = 0.6 \pm 0.1 \tag{2}$$

The experimental exponent is considerably smaller than the value of $m = {}^6/_7$ expected by the scaling theory. The dependence of viscosity on added salt (assuming f is independent of added salt) was found to obey the scaling form at each value of f, but with an apparent exponent that is (barely) smaller than predicted by the scaling theory ($n = 0.70$ instead of $n = {}^3/_4$).

$$\eta \sim \left[1 + \frac{2c_s}{fc}\right]^{-n} \quad \text{with} \quad n = 0.70 \pm 0.05 \tag{3}$$

The term $2c_s/(fc)$ is simply the ratio of salt ions ($2c_s$) and free counterions (fc). Using these two experimentally determined exponents, we can test whether scaling applies to the viscosity of polyelectrolyte solutions by constructing a master curve that includes all data at different salt concentrations and charge densities. This master curve is shown in Figure 2 with $m = n = 0.67$, where we plot specific viscosity as a function of $f^{0.67}[1 + 2c_s/(fc)]^{-0.67}$. Figure 2 clearly shows that all data are reduced to a single straight line, thereby demonstrating the utility of scaling. Plots with the optimal exponents of $m = 0.6$ and $n = 0.70$ in eqs 2 and 3 show even less scatter, but within our experimental error these two exponents are the same (see Figure 2).

The finding that the exponents are smaller in magnitude than expected by the scaling theory may indicate that refinements are needed in that theory. The error bars in eqs 2 and 3 were estimated from the natural scatter of the data, using the criterion that the correlation coefficients stay within 0.999 of their optimum values. The error bars on the exponent n barely reach the theoretical prediction, possibly suggesting that the experimental value of this exponent is slightly lower than predicted. The error bars on the exponent m are broader owing to the limited range of the charge density covered ($0.123 < f < 0.229$). Unfortunately, the only way to extend this range is to study polymers with lower charge density, where complications from acid group dissociation become important.[10,12] The absolute error in f is estimated as ±10%, owing primarily to calibration of the electrode. However, all measurements were made using the same calibration, so the ratios of different f values, relevant for exponent determinations, have much smaller error. Thus, the experimental value for the exponent $m = 0.6 \pm 0.1$ is really lower than the scaling prediction ($m = {}^6/_7$). Dipolar attraction between condensed counterions[13] may account for the lower than expected exponent. Figure 1 clearly shows that condensation of Na^+ counterions occurs in our strongly charged polymers. The condensed ions form dipolar pairs with the acid groups on the polyion, and the attraction between these dipoles[13] can reduce the coil size and lower the viscosity, thereby lowering the apparent exponent m. Such effects were not considered in the scaling approach,[1] and they go beyond the scope of the discussion herein.

The finding that the scaling ideas apply to the charge density and salt concentration dependences of specific viscosity of a weakly charged polyelectrolyte is consistent with the results on a strongly charged polyelectrolyte,[2] where the dependences on polyelectrolyte concentration and salt concentration were tested. In that study, the high salt limit was studied over a wide range of added salt, and the data were consistent with $n = {}^3/_4$. However, the polyelectrolyte concentration dependence of specific viscosity was considerably weaker than predicted by the scaling theory, indicating the possible role of logarithmic corrections to scaling.

Curiously, both studies show that the specific viscosity is insensitive to the overlap concentration. The chains should start to overlap when $\eta_{sp} \cong 1$. Both Figure 2 here and Figure 7 of ref 2 indicate that the same (or indistinguishably similar) scaling applies both above and below the overlap concentration, for viscosity data on solutions with considerable added salt. The high salt limit of polyelectrolytes is in the same universality class as neutral flexible polymers in a good solvent.[14] Neutral polymers in good solvent[15,16] only have a subtle change in their concentration dependence of specific viscosity at c^* ($\eta_{sp} \sim c$ for $c < c^*$, and $\eta_{sp} \sim c^{5/4}$ for $c^* < c < c_e$, where c_e is the entanglement concentration). The scaling theory for polyelectrolyte solution dynamics Dobrynin 1995 predicts similarly subtle changes in dependences of viscosity on other quantities at c^*. For example, for a polyelectrolyte dissolved in a good solvent for the uncharged monomer in the high salt limit, $\eta_{sp} \sim c_s^{-3/5}$ for $c < c^*$, and $\eta_{sp} \sim c_s^{-4/5}$ for $c^* < c < c_e$.

In summary, we have demonstrated that the scaling theory with empirical exponents can describe the viscosity of our poly(acrylic acid) solutions. In particular, the dependence of viscosity on the fraction of charged monomers on the chain f is tested here for the first time. Clearly, a more extensive study of poly(acrylic acid) viscosity, covering wider ranges of c, c_s, and f would be useful. Such a study would require using osmotic pressure to determine f for samples with lower neutralization extents.

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