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Possible Origins of the Friction of Partially Ionized Poly(acrylic acid) Gels

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The compressional osmotic modulus (M) and cooperative diffusion coefficient (D_c) of partially neutralized poly(acrylic acid) gels were measured recently as a function of polymer concentration [c_p (monomers/unit volume)] and degree of ionization (α) at constant temperature.[1] In the absence of salt and when the degree of ionization lies in the range $0.05 \le \alpha \le 0.35$, it is found that $M \propto c_p\alpha$ and (approximately) $D_c \propto \alpha^{1/2}c_p^{-1/2}$.[1] Throughout this regime ($0.05 \le \alpha \le 0.35$) counterion condensation does not occur. From these results it is inferred that the friction coefficient per unit volume of the gel network in the absence of salt varies with c_p and α approximately according to[1]

$$\zeta_{\text{total}} \propto M/D_c \propto c_p^{1.5}\alpha^{0.5} \tag{1}$$

These results are insensitive to the cross-linking degree for a given value of c_p,[2] so in that sense the gel behaves as a semidilute solution.

In principle, the dependence of ζ_{total} on α could arise from the effect of charge on the pore size or correlation length (ξ) of the gel and also from the effect of electrolyte friction[3–6] between the moving fluid, which contains the counterions, and the charged gel. Here we examine the predictions for each kind of effect separately.

(1) Let us first consider the effect of gel pore size. It is assumed that the frictional resistance to flow (ζ_{total}) is proportional to the inverse number of pores per unit area in a cross section of the gel ($1/n_p$) times the frictional resistance of a pore (f_p). The radius of a pore is assumed to be proportional to the correlation length ξ, so $n_p \propto \xi^{-2}$ and $f_p \propto \xi^{-4}$. Hence, when the frictional resistance arises simply from the pore size of the gel

$$\zeta_{\text{total}} \propto \xi^{-2} \tag{2}$$

At present, there exists no satisfactory theory for ξ that is applicable in the present circumstance, namely, concentrated ($c_p \gg c_p^*$) salt-free solutions of partially ionized polymers, wherein the average contour distance between charges (A), the intrinsic persistence length (L_p), and the average distance between monomers ($c_p^{-1/3}$) are all roughly comparable in size and wherein the sites of ionization are not fixed but may redistribute along the chains as they adopt different configurations. The theory of Pfeuty[7] applies only when the charges are fixed, A is large compared to the total persistence length (L_t), and c_p is only slightly greater than c_p^*, none of which holds here. The theory of Odijk[8] applies only when the charges are fixed and $A^{-3} \gg c_p$, where c_p is the number of monomers per unit volume. The latter condition ensures that the contour distance between charges is much less than the average monomer spacing in solution (i.e., $A \ll c_p^{-1/3}$). In such a case, interactions between two segments of the same or different molecules are typically dominated by electrostatic interactions instead of the usual repulsions of neutral segments (between charges). Alas, neither of these conditions holds in the present case. The estimation of ξ may be further obscured by the presence of cross-links and the tendency of the nonionized segments of poly(acrylic acid) to associate to form mesophase structures.[1] In short, one cannot *confidently* proceed beyond eq 2 at this time.

(2) Let us now consider the possibility that the friction coefficient per unit volume is dominated by electrolyte friction rather than pore size. The pertinent arguments are as follows:

(i) Polymer segments within a correlation volume (ξ^3) are assumed to translate in a concerted fashion during long-wavelength density fluctuations. The translational friction on each correlation volume (ξ^3) is assumed to be dominated by electrolyte friction.[3–6]

(ii) Electrostatic screening *in the salt-free gel* is due to the dissociated counterions, so the effective Debye screening parameter (inverse length) is $\lambda \propto (c_p\alpha)^{1/2}$.

(iii) The electrolyte friction on a given correlation volume arises from electric force fluctuations on the charged polymer contained therein due to charge fluctuations in the remainder of the fluid throughout the gel. The friction factor ζ_{el} for *each* correlation volume is calculated by using the formula for a charged gel sphere with radius $a \propto \xi$ in a salt solution with the same screening parameter λ,[3,4] which is expected to apply in the limit $\lambda\xi > 1.0$, i.e., when α is not too small. There results

$$\zeta_{\text{el}} \propto \frac{1}{\lambda a}\left(\frac{Z^2}{a}\right)f_{\text{el}} \propto \frac{1}{(c_p\alpha)^{1/2}\xi}\left(\frac{Z^2}{\xi}\right)f_{\text{el}} \tag{3}$$

where Z is the effective net charge in the correlation volume and f_{el} is the friction factor of the counterions. We employ eq 27 of ref 3, which follows from the work of Harris and Rice,[9] to obtain $Z \propto n\lambda a/(\lambda a)^2 \propto n(c_p\alpha)^{-1/2}\xi^{-1}$, where $n \propto c_p\alpha\xi^3$ is the number of intrinsic polymer charges in the correlation volume. Hence, $Z \propto (c_p\alpha)^{1/2}\xi^2$, and eq 3 gives

$$\zeta_{\text{el}} \propto c_p^{1/2}\xi^2\alpha^{1/2}f_{\text{el}} \tag{4}$$

for each correlation volume ξ. The total friction factor *per unit volume* of the gel is then $\zeta_{\text{total}} = N\zeta_{\text{el}}$, where $N \propto \xi^{-3}$ is the number of correlation volumes per unit volume. Hence

$$\zeta_{\text{total}} \propto c_p^{1/2}\xi^{-1}\alpha^{1/2}f_{\text{el}} \tag{5}$$

Equation 5 differs from eq 2 in two main respects. It depends in a different way on the correlation length ξ (provided ξ is not simply proportional to $c_p^{-1/2}\alpha^{-1/2}$), and it is proportional to the friction factor of the small ions. Thus, the two possible origins of ζ_{total} can be distinguished by measurements of ζ_{total} and ξ under various conditions of c_p and α or by observation of the dependence of ζ_{total} on f_{el} by changing counterions.

The ability of the sites of ionization to move along the chains suggests the following speculation. Consider a semidilute solution of a neutral polymer. Imagine that one adds univalent salt to concentration c_s°, such that the salt dominates the osmotic pressure to give $\Pi \simeq Ac_p^{9/4} + 2kTc_s^\circ \cong 2kTc_s^\circ$. The correlation length ξ of the polymer is, of course, unperturbed. Now take a similar semidilute solution of the same polymer without salt and ionize it until the counterion concentration is $\alpha^{-1}c_p = c_s^\circ$. In this case, the counterions dominate the osmotic pressure, so $\Pi \simeq kT\alpha^{-1}c_p \simeq kTc_s^\circ$. Not only are the dissociated counterions mobile but also the sites of ionization can redistribute themselves over the polymer network. Because the sites of ionization can move along the chains, it is conceivable that they actually maintain a spatial distribution and pair correlation function similar to that of the co-ions of the salt added to the former solution but do not much affect the organization of the chains. That is, for

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relatively weakly ionized polymers, wherein the sites of ionization are mobile, the polymer organization may be largely uncoupled from the distribution of ionic sites that is responsible for the high osmotic pressure. In such a case, one would expect ξ to depend only weakly, if at all, on α and vary with c_p in the manner expected for a semidilute solution of neutral polymers; namely, $\xi \propto c_p^{-3/4}$. With this result, eq 2 for the pore size effect gives $\zeta_{total} \propto c_p^{1.5}$, whereas eq 5 for the electrolyte friction effect yields $\zeta_{total} \propto c_p^{1.25}\alpha^{1/2}f_{el}$. The latter expression agrees well enough with the limited range of experimental data embodied in eq 1 to warrant further investigation of the possible contribution of electrolyte friction to gel friction.

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