Osmotic Pressure of Polyelectrolytes without Added Salt

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ABSTRACT: We have applied scaling theory to published data on the osmotic pressure Π of solutions of the polyelectrolytes sodium poly(styrenesulfonate) (NaPSS) and poly(styrenesulfonic acid) (HPSS) without added salt. The data cover 4 decades of polymer concentration C; molecular weights M range from 20 to 1060 K. Three different concentration regimes are observed. In the low concentration regime, Π depends on molecular weight. In the semidilute regime, scaling predictions are accurately obeyed: Π is independent of M, and the slope of Π vs C is 1.125. In this regime, the dependence of Π on C also agrees well with predictions of the Poisson–Boltzmann cylindrical cell model theory, though only if the linear charge spacing used in the calculations is somewhat less than the structural value. A dramatic increase in osmotic pressure is observed in the concentrated regime. The slope of Π vs C is close to 2.25, the value predicted from scaling theory for semidilute neutral polymer solutions. This suggests that polyelectrolytes may adopt an expanded random-coil chain conformation in highly concentrated solutions without added salt.

Introduction

Polyelectrolyte solutions without added salt are among the most difficult to understand of all physical systems.[1] This is because of the long range of the electrostatic forces and their coupling with polyion conformation. The Poisson–Boltzmann (P–B) cylindrical cell model for salt-free polyelectrolyte solutions accounts fairly well for the thermodynamic and some transport properties observed at low polyion concentrations.[2-6] However, it is not suitable to describe these properties at higher concentrations or to predict how the average dimensions of a polyion change with concentration as the chains deviate from the assumed locally fully stretched conformation.[1] Counterion condensation theory[7] likewise has great value, but is a limiting law valid only in highly dilute solutions, and also does not take polymer shape changes into account.

Scaling theory has been successful in rationalizing the static and dynamic behavior of neutral polymers and of polyelectrolytes with added salt. The pioneering theoretical work of de Gennes et al.[8] has been elaborated by Odijk.[9-11] These theoretical developments have in turn stimulated new experimental studies.[12,13] Several dynamic light scattering studies of polyelectrolytes with added salt have been reported in the literature.[12-21] Koene et al.[14,15] reported a dependence of the cooperative diffusion coefficient D_m on polyelectrolyte concentration C which agrees reasonably well with the theoretical predictions of scaling theory. Wang et al.[19-21] studied polyelectrolyte and salt concentration dependences of the self and cooperative diffusion coefficients in semidilute solutions of sodium poly(styrenesulfonate) (NaPSS) and obtained fair agreement with the scaling relations developed by de Gennes et al. and Odijk. The osmotic pressure Π of semidilute neutral polymers and polyelectrolytes with added salt has been measured as a function of C by several research groups,[22,23] who found a power law dependence with an exponent close to the value predicted by scaling theory. We have recently shown[24,25] that both scaling theory and renormalization group theory can successfully account for the dependences of Π and D_m on C in semidilute solutions with added salt.

In this paper, we show that scaling theory also yields informative results when applied to polyelectrolytes without added salt. We treat published data on the osmotic pressure of salt-free solutions of the polyelectrolytes sodium poly(styrenesulfonate) (NaPSS) and poly(styrenesulfonic acid) (HPSS), over a 10 000-fold range of polyelectrolyte concentration, examining the predictions of both scaling theory and P–B cylindrical cell model theory.

Theoretical Background

We review the scaling theory predictions for osmotic pressure in the semidilute regimes for three cases: neutral polymers, polyelectrolytes with added salt, and polyelectrolytes without added salt. These are compared with the counterion condensation and P–B cylindrical cell model theories which apply in dilute solutions.

In dilute solutions, Π can be expressed in the form of a virial expansion. If truncated at the first order of concentration, the reduced osmotic pressure $\Pi M/cRT$ is given by

$$\Pi M/cRT = 1 + A_2 Mc \tag{1}$$

where M is the molecular weight and c the polymer concentration in g/mL. The second virial coefficient A_2 is

$$A_2 = 4\pi^{3/2}\rho(z)N_A R_F^{\,3}/M^2 \tag{2}$$

where $\rho(z)$ is the penetration function, which is a constant (0.21) in good solvents,[23] N_A is Avogadro's number, and R_F is the Flory radius of the polymer (the radius of a single chain in the good solvent limit), which varies as

$$R_F \sim M^{3/5} \tag{3}$$

The critical concentration c^* stands for the concentration at which the macromolecular chains start to overlap and is defined by

$$c^* \approx M/(4/3)\pi R_F^{\,3} N_A \tag{4}$$

From eqs 1–4, we have

$$\Pi M/cRT = 1 + 1.12(c/c^*) \tag{5}$$

where (c/c^*) is the reduced concentration showing the degree of coil overlapping.

In the scaling approach to the osmotic pressure of neutral polymer solutions in the semidilute regime, according to des Cloizeaux,[26,27] the osmotic pressure should obey the following relation

$$\Pi/RT \approx \Omega(C/C^*) \tag{6}$$

where C is the monomolar concentration of the polymer in solution and Ω is a dimensionless function depending

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only on the ratio C/C^*. In the semidilute solution ($C \gg C^*$) the thermodynamic osmotic pressure should be independent of molecular weight, which implies that Ω should scale as a simple power law $(C/C^*)^m$. Combining eqs 3, 4, and 6, this leads to the expression for osmotic pressure in a semidilute solution:[26,27]

$$\Pi/RT \sim (C/C^*)^{9/4} \tag{7}$$

The scaling prediction is in good agreement with the experimental data on semidilute poly(methylstyrene) solutions.[23]

Odijk[9-11] argued that the same relations should apply to semidilute polyelectrolyte solutions in the presence of added salt, provided the influence of the electrostatic interactions between the fixed charges on the macromolecular chains is taken into account. He considered a Debye–Hückel type of interaction potential between the fixed charges with a screening length κ^{-1}, defined by

$$\kappa^2 = 8\pi QI \tag{8}$$

where I is the ionic strength and the Bjerrum length Q is defined by

$$Q = e^2/\epsilon kT \tag{9}$$

where e is the elementary charge, ϵ the dielectric constant of the solvent, and kT is the thermal energy. It has been shown[9-11,28,29] that the total persistence length L_t of the charged macromolecules may be approximated by a sum of two terms: the intrinsic persistence length L_p and the electrostatic persistence length L_e

$$L_t = L_p + L_e = L_p + (Q/4\kappa^2 A^2 f^2) \tag{10}$$

where A is the linear charge spacing along the chains and f accounts for the effective charge on the polyelectrolyte chain. According to counterion condensation theory,[7] $f = 1$ if $A > Q$ and $f = Q/A$ if $A < Q$. Odijk gave the osmotic pressure of semidilute polyelectrolytes in the presence of added salt by

$$\Pi/RT \sim (L_t/\kappa)^{3/4}(AC)^{9/4} \tag{11}$$

This scaling prediction is in good agreement with the experimental data on semidilute sodium poly(styrenesulfonate) solutions with added salt.[22,25]

The scaling approach to polyelectrolyte solutions without added salt by de Gennes et al.[8] distinguished three concentration regimes. At the lowest concentrations, the charged macromolecules are on average widely separated, and when characterized by high charge densities, they will be fully stretched if not effectively screened. Above a certain critical concentration, the more or less stretched polyions eventually form a tridimensional lattice. In semidilute solutions, the regime most readily accessible to experimental observation, there is considerable overlap between chains. This leads to a transient network with a characteristic mean distance (correlation length) between adjacent chains which decreases with increasing concentration as $C^{-1/2}$. In semidilute polyelectrolyte solutions without added salt, the electrostatic energy per monomer is of order kT. The osmotic pressure contributed from the polyions scales like the free energy per unit volume and is thus of order

$$\Pi/RT \sim C \tag{12}$$

(Note that this is dimensionally comparable to the counterion pressure.) Odijk considered Debye–Hückel screening as being caused by uncondensed counterions only ($A < Q$)

$$\kappa^2 = 4\pi AC \tag{13}$$

The Debye length is now dependent on C. For the osmotic pressure, eqs 11 and 13 are combined to yield the scaling relation.[11]

$$\Pi/RT \sim 10A^{3/8}C^{9/8} \tag{14}$$

The relation is similar to eq 12 given by de Gennes et al.[8]

Manning has derived an expression for the osmotic pressure of polyelectrolytes without added salt from his condensation theory.[7] For the polyions considered in this paper, which have charge density parameter $\xi = Q/A > 1$, the osmotic pressure is given by

$$\Pi/RT = \Phi C \tag{15}$$

$$\Phi = (2\xi)^{-1} \tag{16}$$

where Φ is the osmotic coefficient of a polyelectrolyte solution under salt-free conditions.

The P–B cylindrical cell model theory can be used to obtain the concentration dependence of the osmotic coefficient.[4] The theory, slightly modified[5] to take account of polyion–counterion excluded volume, gives

$$\Phi = (1 - \beta^2)(2\xi)^{-1}(1 - e^{-2\gamma}) \tag{17}$$

where β is a constant defined by

$$\xi = (1 - \beta^2)/(1 + \beta \coth \beta\gamma) \tag{18}$$

and the concentration parameter γ is connected with the monomolar polyion concentration C by

$$\gamma = \frac{1}{2} \ln \frac{10^3}{\pi b^2 A N_A} - \frac{1}{2} \ln C \tag{19}$$

where b is the radius of the polyions and N_A is Avogadro's number. These counterion condensation and cylindrical cell model expressions have been most extensively used to explain the osmotic pressure of polyelectrolyte solutions without added salt.

Analysis of Experimental Data

We now apply the theoretical approaches outlined above to data in the literature on salt-free, aqueous solutions of sodium poly(styrenesulfonate) (NaPSS) and poly(styrenesulfonic acid) (HPSS). Molecular weights ranged from 2 000 to 1 060 000 and polyelectrolyte concentrations from 3.0×10^{-4} to 4.3 M (polymer monomole/1000 mL). Osmotic pressures were obtained from the product of the measured osmotic coefficients and polymer concentrations in molality. However, since in theoretical work polymer concentrations are expressed in molarity rather than molality, polymer concentrations were converted to molarity via the experimental partial molal volume[30,31] before Π/RT vs C plots were made. The osmotic coefficients were determined by various osmometric and cryoscopic methods in the dilute and semidilute regimes and by the isopiestic method in the concentrated regime. The osmotic coefficients measured by these different techniques agree well. In the case of HPSS, the authors took care to avoid degradation of the sample during the course of the measurements.[32,33]

Osmotic Pressure in Dilute and Semidilute Solutions. A plot of log Π/RT vs log C for NaPSS without added salt at monomolar polyion concentrations from 3.0×10^{-4} to 1.0 M for more than ten different molecular weights ranging from 20 000 to 1 060 000 is shown in the upper points in Figure 1. The experimental data were

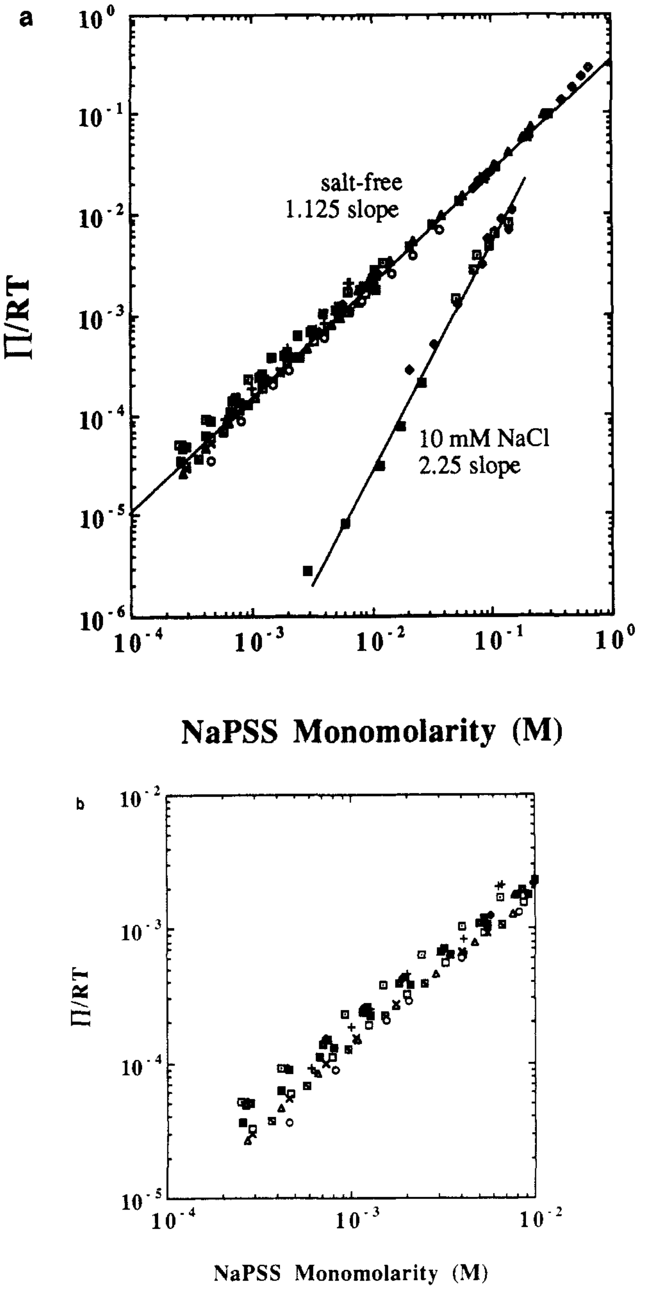

Figure 1. a. The reduced osmotic pressure Π/RT as a function of the polyelectrolyte concentration C in monomol/L for various molecular weight NaPSS in semidilute solutions. b. An enlargement of the low-concentration region, to enable easier identification of individual data points. Experimental data of osmotic pressure without added salt (upper) are taken from Oman,[34,35] Takahashi et al.,[36] Kozak et al.,[37] Vesnaver and Skerjanc,[38] and Marinsky and co-workers.[32,33] The line has the 1.125 slope predicted from scaling theory (eq 14). Experimental data with added salt (lower) are taken from Koene et al.[22] and Takahashi et al.[36] The line has the 2.25 slope predicted from scaling theory (eqs 7 and 11). The molecular weight of NaPSS under salt-free conditions is 2×10^4 (⧈), 3.5×10^4 (♦), 3.7×10^4 (■), 4.0×10^4 (▲), 7.0×10^4 (■), 8.0×10^4 (+), 1.2×10^5 (□), 1.6×10^5 (×), 3.05×10^5 (△), 3.2×10^5 (○), 5.0×10^5 (◇), and 1.06×10^6 (⧅). Molecular weight of NaPSS in 0.01 M NaCl solution is 1.2×10^6 (♦), 4.0×10^5 (■), 6.5×10^5 (⧈), and 3.2×10^5 (■).

taken from Oman,[34,35] Takahashi et al.,[36] Kozak et al.,[37] Vesnaver and Skerjanc,[38] and Reddy and Marinsky.[32] The overlap concentration C^*, calculated from $C^* = (16\pi Q \times AL)^{-1}$, where L is the contour length of the polyion[1,11,39] ranges from 7.6×10^{-3} M for molecular weight 20 000 to 1.4×10^{-4} M at molecular weight 1.06×10^6. Over the low polymer concentration range, approximately up to the overlap concentrations for these different molecular weights, the plot shows considerable scatter. This is a manifestation of the expected molecular weight dependence of the reduced osmotic pressure in the dilute solution regime: low molecular weight polyions give higher Π. The upper straight line in Figure 1 has the slope of 1.125 predicted from scaling theory for the semidilute regime (eq 14). The experimental data are in good agreement with this prediction, typically with a slope in the range 1.10–1.15, with a standard error of ±0.01. The slope of 1.0 predicted from eq 12 significantly underestimates the experimental slope. The numerical coefficient of 10 in eq 14 also is in reasonable agreement with the experimental values, which range from about 10 to 20 depending on which data set is analyzed. The lack of molecular weight dependence in the high C range, beyond the overlap concentration, also satisfies the scaling theory prediction for the semidilute regime.

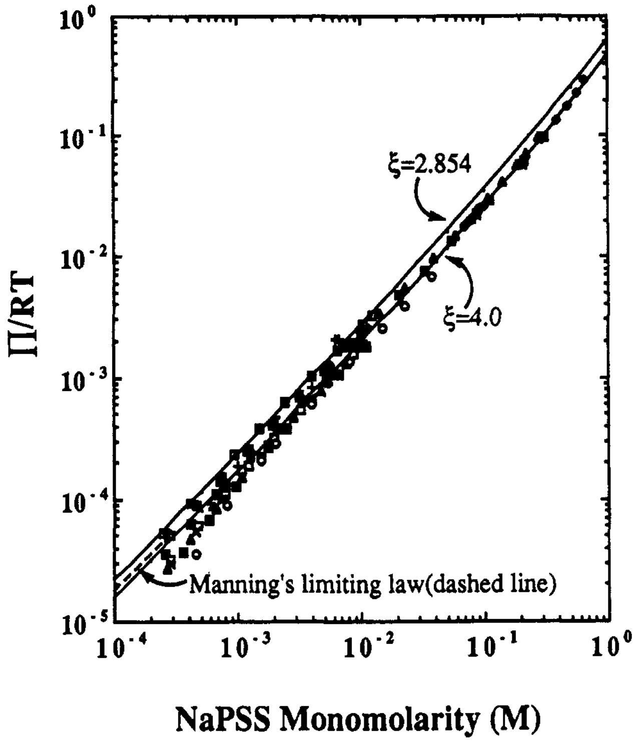

Figure 2. The reduced osmotic pressure Π/RT as a function of the polyelectrolyte concentration C in monomol/L for various molecular weight NaPSS in semidilute solutions without added salt. Experimental data are the same as in Figure 1. The upper line is calculated from eqs 15–19 based on b = 8 Å and A = 2.5 Å, giving the structure value of $Q/A = \xi = 2.854$. The lower line is calculated with $\xi = 4.0$. The value predicted from Manning's limiting law (eqs 15 and 16) is indicated by a dashed line.

The lower set of points in Figure 1 is for NaPSS in 0.01 M NaCl.[22,36] Data are given for four different molecular weights, in the range 3.2×10^5 to 1.2×10^6. The 2.25 slope predicted from scaling theory (eqs 7 and 11) is drawn through these points. Agreement is excellent. NaPSS solutions with added salt have lower osmotic pressures than salt-free solutions, as expected from comparison of eqs 11 and 14, which arise from the different assumed conformations—flexible random coil and wormlike chain—in the two types of solutions.

The data on NaPSS are compared in Figure 2 with the predictions of counterion condensation (eqs 15 and 16) and P–B cylindrical cell model theories (eqs 17–19). The upper line is calculated with polyion radius b = 8 Å

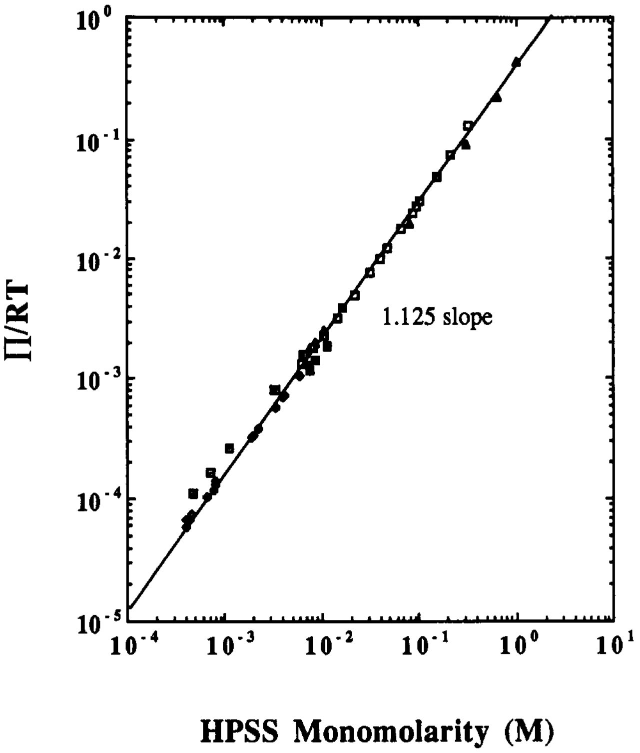

Figure 3. The reduced osmotic pressure Π/RT as a function of the polyelectrolyte concentration C in monomol/L for various molecular weight HPSS in semidilute solutions without added salt. Experimental data are taken from Oman,[34,35] Kozak et al.,[37] and Marinsky and co-workers.[32,33] The line has the 1.125 slope predicted from scaling theory (eq 14). Molecular weight of NaPSS is 3.5 × 10^4 (⊡), 3.7 × 10^4 (♦), 4.0 × 10^4 (□), 1.77 × 10^5 (♦), 3.05 × 10^5 (■), and 5.0 × 10^5 (▲).

and charge spacing $A = 2.5$ Å, values thought to be close to the structure of NaPSS. This value of A gives $\xi = 2.85$. Better agreement with experiment is obtained with $\xi = 4.0$, which yields the lower curve. The predicted value from Manning's limiting law with $\xi = 2.85$ is also indicated in Figure 2. With the adjusted ξ, both theories give good agreement with experiment in the low and semidilute concentration regimes. However, they somewhat overestimate the experimental values in the very low concentration region, as was noted in Manning's original paper[7] and in more recent work.[34,35,37]

A plot of log Π/RT vs log C for HPSS without added salt at polyion concentrations from 3.0 × 10^{-4} to 0.1 M for six different molecular weights ranging from 35 000 to 500 000 is shown in Figure 3. The experimental data were taken from Oman,[34,35] Kozak et al.,[37] and Reddy and Marinsky.[32] The 1.125 slope predicted from scaling theory is in good agreement with the data. As with NaPSS, a molecular weight dependence of Π/RT is evident at low polymer concentration. It has been reported that the pure acid form of HPSS in aqueous solution is completely dissociated.[40,41] Therefore, the only difference between HPSS and NaPSS should be the radius of the counterion, which has little effect on the osmotic pressure of polyelectrolyte solutions without added salt.[3,4,37]

Osmotic Pressure in Concentrated Solutions. The concentration dependence of the osmotic pressure increases dramatically in the concentrated solution regime. Figures 4 and 5 show log Π/RT vs log C for NaPSS and HPSS under salt-free conditions at polyion concentrations from 0.7 to 4.3 M for five different molecular weights ranging from 10 000 to 500 000. The experimental data were taken from Bonner and Overton[42] and Reddy and Marinsky.[32] The results (not shown) of Waxman et al.[43] for HPSS are also consistent with the data in Figure 5. The straight lines in both figures have slopes of 2.25. This slope is not predicted by scaling theory for salt-free polyelectrolyte solutions.[8,11] However, a 2.25 slope was predicted for neutral polymer solutions and polyelectrolyte solutions with added salt (eqs 7 and 11).

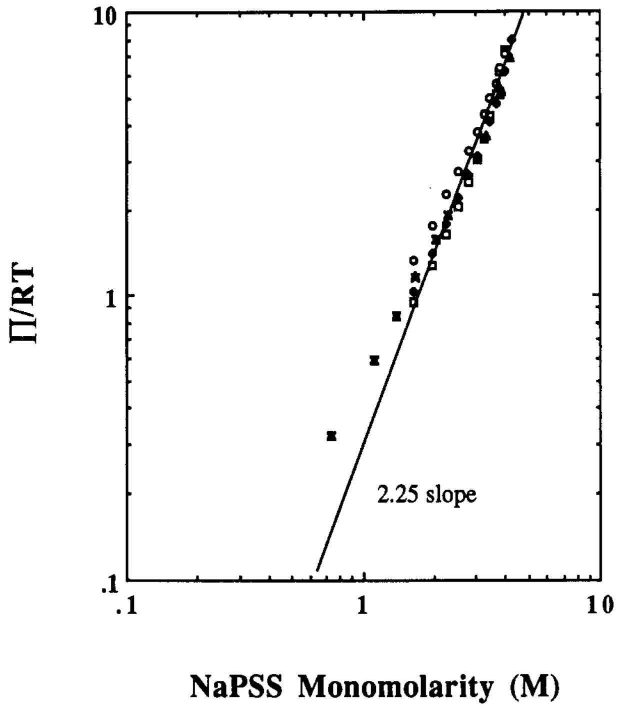

Figure 4. The reduced osmotic pressure Π/RT as a function of the polyelectrolyte concentration C in monomol/L for various molecular weight NaPSS in concentrated solutions without added salt. Experimental data of osmotic pressure without added salt are taken from Bonner and Overton[42] and Reddy and Marinsky.[32] The straight line has a slope of 2.25. Molecular weight of NaPSS is 1.0 × 10^4 (□), 4.0 × 10^4 (×), 7.0 × 10^4 (♦), 4.0 × 10^5 (○), and 5.0 × 10^5 (▲).

A reviewer has pointed out that if a hard-core repulsion of diameter b is allowed for, eq 11 would have a form approximating

$$\Pi/RT \sim L_t^{3/4}(b + \kappa^{-1})^{3/4}(AC)^{9/4} \qquad (20)$$

This is obtained by adding b to the "electrostatic diameter" or Debye length κ^{-1}, an idea which has been implemented with greater rigor (and more complicated but qualitatively similar results) by Onsager[44] and Stigter.[45] Since κ^2 is proportional to the monomolar concentration C, eq 20 has the proper slopes of 9/8 at intermediate C and 9/4 at very high C. Since κ^{-1} is about 10 Å at 0.1 M ionic strength and 3 Å at 1 M, if b is about 8 Å the crossover would be about 1 monomolar as shown in Figures 6 and 7.

In solutions of neutral polymers and polyelectrolytes with added salt, the polymer chains have a random coil conformation in the good solvent limit. These results therefore suggest that polyions also adopt a random coil conformation in salt-free solutions, if the polymer concentration is high enough. To prove this conjecture, radius of gyration (R_g) data would be valuable. Some partial data indicating its validity are available. Nierlich et al.[46] measured R_g as a function of polymer concentration for deuterated NaPSS (M = 26 000) in salt-free semidilute hydrogenated solutions by small angle neutron scattering. At low polymer concentrations (0.0817 M), R_g was close to that of the totally stretched rodlike chain. At high polymer concentration (0.563 M), R_g approached that

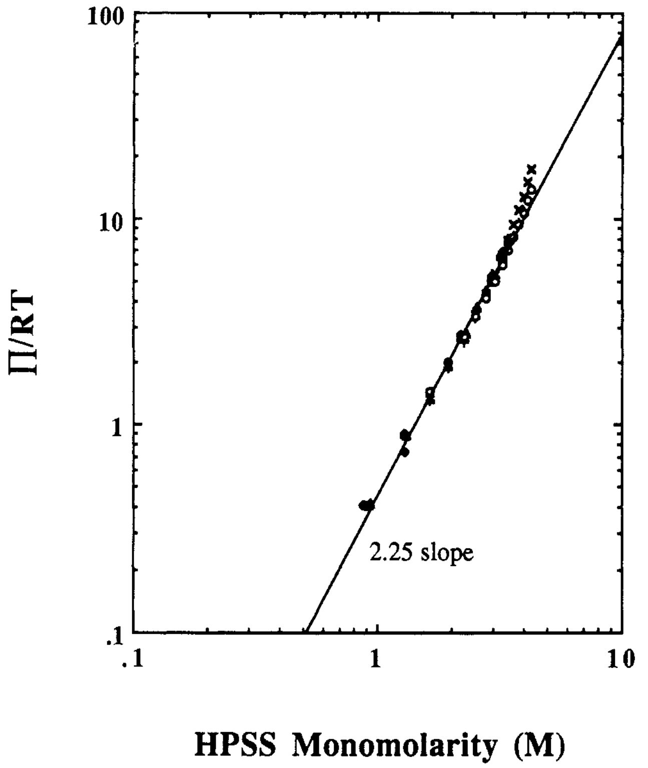

Figure 5. The reduced osmotic pressure Π/RT as a function of the polyelectrolyte concentration C in monomol/L for various molecular weight HPSS in concentrated solutions without added salt. The experimental data were taken from Bonner and Overton[42] and Reddy and Marinsky.[32] The straight line has a slope of 2.25. Molecular weight of NaPSS is 1.0×10^4 (×), 4.0×10^4 (♦), 7.0×10^4 (+), 4.0×10^5 (○), and 5.0×10^5 (▲).

of the parent polystyrene under Θ conditions. Unfortunately, R_g were not measured at even higher polymer concentrations or with a longer polymer chain, where the random-coil R_g might have been reached.

Conclusions

Our results show that there are three reasonably distinct regimes for the dependence of osmotic pressure on concentration for polyelectrolyte solutions without added salt. These are summrized in Figures 6 and 7 separately for NaPSS and HPSS. There are not sharp breaks between these regions, but each extends over an appreciable concentration range, justifying their separate identification. Callaghan and Pinder[47] have questioned the existence of a unique length scale in semidilute solutions, on which scaling theory rests. Notwithstanding this critique, the scaling approach has led to useful insights in both neutral and polyelectrolyte solutions, including those considered here.

The molecular weight dependent behavior at low polymer concentrations corresponds to the transition from the dilute to the semidilute regime. In the semidilute regime, the molecular weight independence and slope of the log–log plot of Π/RT vs C are in excellent agreement with the predictions of scaling theory. The osmotic pressures of these semidilute solutions are also in good agreement with the values calculated from the P–B cylindrical cell model theory. The transition from the semidilute to the concentrated regime occurs at around 1.0 monomolar polymer concentration. This transition is not dependent on molecular weight of polyions and also is not indicated in the phase diagram constructed by Kaji et al.[48] for polyelectrolyte solutions. A dramatic increase in osmotic pressure is observed in the high concentrated regime. The power of the dependence of Π on C is close to 2.25, the value predicted from scaling theory for semidilute *neutral* polymer solutions. This suggests that an

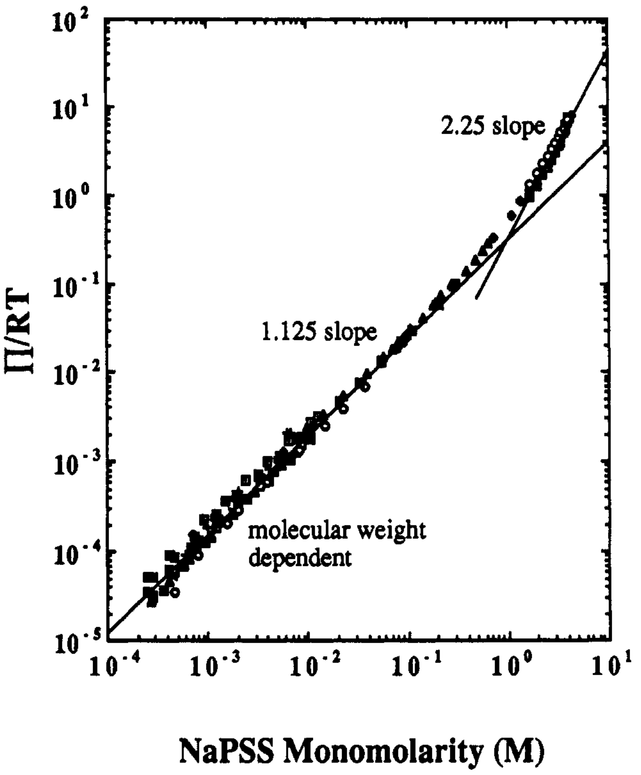

Figure 6. The reduced osmotic pressure Π/RT as a function of the polyelectrolyte concentration C in monomol/L for various molecular weight NaPSS in salf-free solutions, combined from Figures 1 and 4 to emphasize the three concentration regimes.

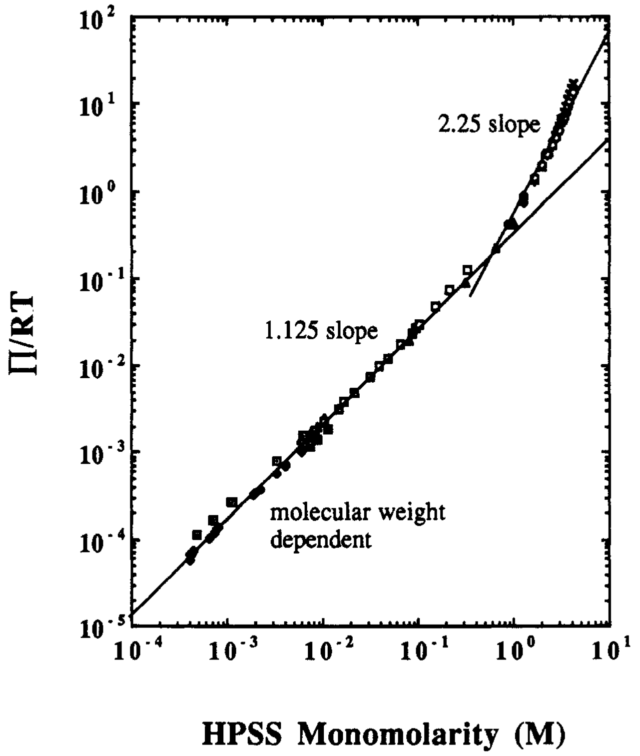

Figure 7. The reduced osmotic pressure Π/RT as a function of the polyelectrolyte concentration C in monomol/L for various molecular weight HPSS in salt-free solutions, combined from Figures 3 and 5 to emphasize the three concentration regimes.

expanded coil conformation of the sort adopted by neutral polymers in good solvents may be reached in highly concentrated polyelectrolyte solutions without added salt.

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Hydrodynamic Interaction Effects on the Conformation of Flexible Chains in Simple Shear Flow

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ABSTRACT: The deformation of polymers modeled as bead-and-spring chains in simple shear flow is studied by Brownian dynamics simulation including hydrodynamic interaction (HI) effects. Previous theories neglecting HI, which are confirmed by our simulations, predicted that deformation scales with N^4, where N is the number of polymer units. Our results with nonpreaveraged HI give also an exponent of roughly 4, although the deformation is about half that predicted neglecting HI. Comparison with experimental data is made. We also discuss the utility of the dumbbell model for the representation of flexible polymers and the relative importance of spring stretching and alignment in the deformation of the chain.

Introduction

The theoretical study of the behavior of polymer chains under solvent flow presents difficulties, most of which are due to the hydrodynamic interaction (HI) between chain elements. Thus, it is usual to neglect hydrodynamic interaction effects in analytical calculation of rheological properties.[1] In some instances, hydrodynamic interactions can be introduced in an averaged form. Thus the theories are able to make qualitative or semiquantitative predictions that are quite useful. However, in some cases, the properties are quantitatively influenced, to a significant extent, by hydrodynamic interactions. In a recent paper,[2] we have shown that hydrodynamic interaction effects can be studied by computer simulation of the Brownian dynamics of the polymer chain in a flowing solvent.

In our previous study, we considered the most simple and common model in polymer rheology, the elastic dumbbell, in a simple shear flow. We evaluated, as a function of shear rate, the dumbbell extension, which mimics the end-to-end distance of the polymer molecule, and the components of the stress tensor. Apart from its evident influence on material properties, we detected that nonpreaveraged HI modified appreciably the square end-to-end

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