Stiff (DNA) and Flexible (NaPSS) Polyelectrolyte Chain Expansion at Very Low Salt Concentration[†]

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ABSTRACT: The expansion of sodium poly(styrenesulfonate) (NaPSS) polyelectrolyte coils has been studied by light scattering and velocity sedimentation at a NaCl concentration of 0.5–0.001 M. Good agreement between the flexible NaPSS and intrinsically stiff DNA (data from a previous study) is obtained in terms of the conformation-space renormalization-group approach. Present polyelectrolyte expansion and excluded-volume theories are not adequate to satisfactorily interpret the experimental results.

I. Introduction

When electrically charged groups are attached to flexible polymer chains creating a polyelectrolyte,[1] chain expansion occurs as monitored by increasing reduced specific viscosity η_{sp}/c and radius of gyration R_g and decreasing sedimentation s and translational diffusion D coefficients.[2,3] In the presence of added simple electrolytes, electrostatic charges are screened, chain expansion is reduced, and Flory Θ dimensions and even phase-separation characteristics of nonionic polymer solutions[4] can be achieved.[5,6] A polyelectrolyte ion $P^{n(+)}$ or $P^{n(-)}$ with counterion nX^- or nX^+ (component 2) dissolved in water (component 1), containing a simple electrolyte X^-Y^+ or X^+Y^- (component 3), constitutes a three-component system which can be analyzed subject to the laws of the thermodynamics of multicomponent systems.[7,8] However, counterions and co-ions need not be monovalent. If the solutions are dilute enough with respect to component 2 and the simple electrolyte concentration component 3 is high enough, then properties corresponding to single macromolecules (η_{sp}/c, R_g, s, D) can be derived, as well as the molar mass M_2 of the particles and interaction parameters such as the virial coefficients, A_2. If the salt concentration is strongly reduced, then the polyelectrolyte chains expand significantly, electrostatic forces become longer ranged, and at some stage in the process it becomes difficult to associate measured quantities with the properties of single molecules. In the absence of added simple electrolyte, although the system reduces to two components only, comparable to a nonionic polymer in a nonionic solvent, one can only consider its properties in a broader context, since the nonscreened long-range electrostatic charges do not allow the use of virial expansions and analysis in terms of individual macromolecules. Experimental studies of polyelectrolytes ostensibly undertaken at salt-free conditions must be viewed with great suspicion as ion-free conditions can hardly be realized in aqueous solutions. Furthermore, whereas expansion of polyelectrolytes is an accepted phenomenon, the limits of the expansion have never been properly established.[9]

To overcome the expanding range of long-range electrostatic forces at very low salt concentrations, it is necessary to reduce the polyelectrolyte concentration to limits beyond which signal-to-noise ratios become seriously limiting factors in most practical experiments. Thus, whereas η_{sp}/c of nonionic polymers decreases with decreasing polymer concentrations, η_{sp}/c of polyelectrolytes in "salt-free" solutions increases strongly with decreasing polymer concentration, which led to the formulation of the Fuoss polyelectrolyte viscosity equation,[10] implying polyelectrolyte expansion to rodlike fully extended dimsions at vanishing polyelectrolyte concentrations. However, we could show that, at low enough polyelectrolyte concentrations and at suitably low rates of shear, η_{sp}/c reaches a maximum and decreases with a further decrease in the polyelectrolyte concentration.[11] Very small amounts of added simple electrolytes restore the ability to analyze the η_{sp}/c concentration dependence in terms of a single molecule expansion.[11] More recently, the described behavior has been analyzed in terms of transitions from an ordinary to an extraordinary phase and much confusion prevails as can be judged from a recent publication.[12] Polyelectrolyte solutions have been divided into dilute, semidilute, and concentrated domains.[13] In our present contribution we restrict our interest to the dilute, ordinary polyelectrolyte regime only, aiming at establishing, with the use of light scattering techniques, the correct limits of expansion of polyelectrolyte coils at low salt and low polyelectrolyte concentrations. We shall also try to estimate the limits of the validity of polyelectrolyte theories proposed in recent years.

When polyelectrolyte theories were first presented,[14,15] it became a pioneering challenge to combine the theories of random coil expansion and contraction of nonionic polymers with energy terms deriving from the electrostatic interactions to calculate dimensions of polyelectrolyte coils as a function of charge density and simple electrolyte concentration. It is not appropriate here to go into a detailed discussion of early polyelectrolyte theories, which have been reviewed,[2,3] but suffice it to say that the influence of the electrostatic potential was highly overrated and the prediction that in most circumstances polyelectrolyte coils would expand to full linear extension in solution was not confirmed.[11] Experimental difficulties, as already mentioned, had to be overcome, and special equipment was designed to measure viscosities, for instance, at unusually low rates of shear[16] or scattering of light at low scattering angles.[17] In another effort to evaluate coil expansion, polymer chains were connected into a three-dimensional macroscopic network, charges appended by ionization[18] or chemical treatment,[19] and the volume of the cross-linked polyelectrolyte chains determined in thermodynamic equilibrium with different electrolyte solutions. The feeling evolving from a variety of experiments confirmed the preliminary understanding that the dimensions of polyelectrolytes, at even the highest achievable charge densities and lowest concentrations of added electrolytes,

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[†] This work is dedicated to honor the memory of Charles Sadron, who pioneered DNA and synthetic polyelectrolyte research half a century ago in Strasbourg, in the Institute carrying his name.

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do not reach maximum extensions corresponding to stretched polyelectrolyte rods. Thus, it appears that the restoring force deriving from Brownian entropy motion was sufficient to balance electrostatic expansion tendencies, leading to intermediate expanded conformations. The problem has not been satisfactorily solved to date, and recent developments will be presented below. When it became clear in the early days of polyelectrolyte research that correct polyelectrolyte expansions could not be easily calculated, theoretical concepts veered into considerations based on the valid hypothesis that over short distances an expanded polyelectrolyte chain can be attributed "rodlike" symmetry and a number of interesting phenomena, such as activity coefficients of counterions, "condensation" of counterions, potentiometric titrations, and conductance, can be solved by solutions relating to the Poisson–Boltzmann equation for cylindrical rod symmetry.[20–24] This approach obviously excludes all considerations leading to the determination of chain expansion over larger distances, an idea erroneously attributed to it in some recent publications. Fashionable current scaling theories[25] can also only make *ad hoc* assumptions in the prediction of polyelectrolyte expansion without providing a solid basis for reliable quantitative evaluations.

In simple-electrolyte solution lore, a story was told that Peter Debye was upset by a lecture by I. C. Ghosh, who believed that, in modern parlance, the activity of simple electrolytes "scaled" with the cube root of electrolyte concentration. Debye therefore introduced the concept of the ionic "atmosphere" which led in simple fashion to the correct "scaling" of the activity coefficients with the square root of the ionic concentration.[26] No successful scaling approach has so far been established for the analysis of polyelectrolyte systems.

In early attempts to analyze the expansion of polyelectrolyte coils, the reference state for the expansion coefficient α was considered to be the conformation of the polyelectrolyte molecule in the experimentally accessible Θ state.[27] In an attempt to better rationalize the expansion, Odijk and Houwaert[28] introduced the concept of the additivity of the bare persistence length L_p with an electrostatic persistence length L_e to yield the total persistence length L_t in a wormlike polyelectrolyte chain model. They calculate L_e to scale with reciprocal of the ionic strength, yet from a range of experimental results[29] a reciprocal square root dependence was claimed to be more likely closer in line to the Le Bret[30] and Fixman[31] analyses. We doubt the applicability of strict scaling laws as will be shown by the analysis of experimental results of two typical polyelectrolytes, DNA and the Na^+ salt of poly(styrenesulfonic acid) (NaPSS). Odijk[32] analyzes intrinsic viscosity data of DNA, using an arbitrary value L_p = 600 Å, and Stigter[33,34] analyzes some of the same DNA data with a value L_p = 425 Å. We have determined L_p = 285 Å for DNA in Θ conditions,[35] a value we will use in our present work. Le Bret[30] claims reasonable agreement of his theory with L_e values of DNA calculated from light scattering results reported by us,[36] without indicating the value of L_p used by him. A reliable analysis of theoretical attempts to interpret polyelectrolyte expansion data seems to be lacking.

One of us (H.E.) recalls a conversation in September 1957 with Lars Onsager at a General Discussion in Oxford of the Faraday Society on Interaction in Ionic Solution. Onsager stated then that the mathematics required for the solution of the polyelectrolyte problem were not yet available. Maybe this statement can be modified with the advent of powerful computing systems, yet Monte Carlo calculations, which may lead to a better analysis, are still restricted to relatively short chains. Recent studies in this field of activity are available and have been listed.[37] In an interesting contribution[38] serious thoughts are expressed concerning basic factors to be considered in future more trustworthy polyelectrolyte expansion calculations. Present Monte Carlo calculations[38] on short chains qualitatively confirm the concept derived from experiment that polyelectrolyte chains do not expand to fully stretched conformations.

A topic of great interest in the study of the expansion of polyelectrolyte chains is the contribution of the excluded volume to polyelectrolyte dimensions. Chain dimensions are increased beyond local structural and electrostatic stiffening by volume exclusion, derived from nonelectrostatic and electrostatic interactions, between distant elements along the polymeric chain. The excluded volume of nonionic polymers vanishes when the second virial coefficient A_2 vanishes and Flory Θ dimensions are achieved.[4] This concept is based on equalizing the effect of intra- and intermolecular nonideality, a concept which may not apply in its entirety to polyelectrolyte solutions. Polyelectrolyte solutions have been studied at vanishing values of A_2,[27,35,39,40] and values of L_p can be estimated. At low salt concentrations, away from Θ conditions, experimental values such as the radius of gyration R_g for instance, determined by light scattering, should be corrected for excluded volume to obtain experimental values of L_e. Corrections for excluded volume have been obtained by extension[28,34] of the classical analysis[41] of polymer solutions or by use of Monte Carlo analysis.[42] We shall discuss this below.

Some experimental progress was made following the synthesis of uniformly sized polyelectrolytes[43,44] and progress in the development of sophisticated experimental approaches, of which static and dynamic light scattering proved to be the most appropriate.[45] A favorite natural polyelectrolyte, deoxyribonucleic acid (DNA), was much studied with respect to configurational properties in solution[46] and here as well progress could be achieved by the more recent studies of various forms of uniform sizes of this vital material.[47,48] DNA is a naturally extremely stiff, hydrogen-bonded, charge-carrying double helix, lacking the flexibility of single electrolyte chains. Measurements at very low ionic strengths are limited by the fact that, at low salt concentrations (around 1 mM NaCl), DNA becomes unstable and separates into single strands. Single-stranded polyribonucleic acid chains (RNA) are essentially less stable and more difficult to handle.

In the present study, we have examined the expansion of a uniformly sized sample of NaPSS over a broad range of NaCl concentrations by light scattering and velocity sedimentation, determining M_2, A_2, R_g, D, and s. We confirm that the expansion of the polyelectrolyte coils is far from fully completed at the lowest salt and polyelectrolyte concentrations, which could be experimentally handled in the "dilute" concentration regime, and we present our data in the context of recent theoretical attempts. It is not excluded that in appropriately selected "semidilute" conditions a phase transition might lead to aligned, extended chains, yet this is beyond our avowed intention in the present work of determining the spatial expansion of "single" polyelectrolyte coils, unaffected by the "short" range or "long" range presence of surrounding chains. Below, we compare the behavior of the flexible, synthetic polyelectrolyte with results earlier obtained[36,49] for the intrinsically much stiffer DNA coils.

II. Materials and Methods

Sodium poly(styrenesulfonate), purchased from Pressure Chemical Co. (Pittsburgh, PA), had a molar mass of 10^6 g/mol, with $M_w/M_n < 1.1$ according to the manufacturer. We accepted a degree of sulfonation close to unity following Koene and Mandel.[50] Light scattering and sedimentation measurements in the Beckman Model E analytical ultracentrifuge were performed as previously described.[45,47,49] For the determination of the diffusion coefficient, the prescaled clipped[45,47,49] autocorrelation functions of the scattered light fluctuations were computed with a Malvern RR95 unit and the accumulated data were analyzed using a cumulant fit. A single-exponential fit with a decay time τ yields an apparent diffusion coefficient D_{app} given by

$$D_{\mathrm{app}} = 1/2\tau q^2 \qquad (1)$$

where $q = (4\pi n/\lambda)\sin(\theta/2)$, n is the solvent refractive index, θ is the scattering angle, and $\lambda = 514.5$ nm is the wavelength of the incident light. The experimental values of $D_{20,\mathrm{sol}}$ were obtained by extrapolation to $c_2 = 0$ and $\theta = 0$, the concentration c_2 is in g/mL. The correctness of these data was confirmed by use of a 64-channel with 8 delayed channels Langley–Ford Model 1096 correlator. Light scattering measurements[47] were collected in the angular range 12–150°, and the NaCl concentration was varied between 0.5 and 0.001 M.

The extinction coefficient at $\lambda = 261.5$ nm in water, used for concentration determination, was determined to be 1.75 mL/mg for KPPS[43] and varies somewhat with salt concentration. Multiplication by the monomolar mass ratios 222/206 yields 1.89 mL/mg for NaPSS in water.

Refractive index increments $(\partial n/\partial c_2)_\mu$, at constant chemical potential μ of diffusible solutes,[7,8] were previously[39,43] determined to be 0.156 mL/g in 2.5 M KCl at $\lambda = 546$ nm and close to 0.180 mL/g at $\lambda = 546$ nm and 0.186 mL/g at $\lambda = 436$ nm between 0.5 M and 1 mM KCl. From these values we calculate[51] 0.184 mL/g at the laser wavelength $\lambda = 514.5$ nm for KPSS corrected to 0.198 mL/g for NaPSS, between 0.5 M and 1 mM NaCl.

For the evaluation of sedimentation experiments in multicomponent systems, density increments $(\partial\rho/\partial c_2)_\mu$ are required.[7,8] We believe the values of $(\partial\rho/\partial c_2)_\mu$ determined by Raziel and Eisenberg[39] are too high. Carroll and Eisenberg[43] determined $(\partial\rho/\partial c_2)_\mu = 0.289$ mL/g in 2.5 M KCl, and we determined $(\partial\rho/\partial c_2)_\mu = 0.287$ mL/g in a Kratky/Paar densitometer, following careful dialysis in 0.1 M NaCl.

III. Radius of Gyration from Light Scattering

From the concentration and angular dependence of the intensity of scattered light, it is possible to determine second virial coefficients A_2 and radii of gyration R_g by the Zimm plot[52] if the concentrations correspond to the dilute solution range which, for coiling macromolecules, approximates to

$$c_2 < M/R_g^{\,3}N_{\mathrm{Av}}(2^3)(5/3)^{3/2}\ \mathrm{g/mL} \qquad (2)$$

where N_{Av} is Avogadro's number and R_g is in centimeters. For the obtainment of linear Zimm plots, yielding R_g independent of the molecular nature of the macromolecules (spheres, Gaussian coils, or rods), the linear dimensions of the particle should not exceed $\lambda/20$. For polyelectrolyte coils expanded by electrostatic repulsions, the lower limit of scattering angles accessible in our light scattering experiments ($\theta \sim 12°$), linear Zimm plot expansions, limited in range to $0 < q^2R_g^{\,2} < 0.3$, are not accessible. Fortunately, it was noted[17] that for values $q^2R_g^{\,2} < 2$ the angular dependence of scattering of Gaussian random coils, wormlike coils with excluded volume, and stretched rods is identical, considerably extending the range of the validity of the linear Zimm plot. Correct R_g values could thus be obtained in our study, in the range in which the above criterium was satisfied.

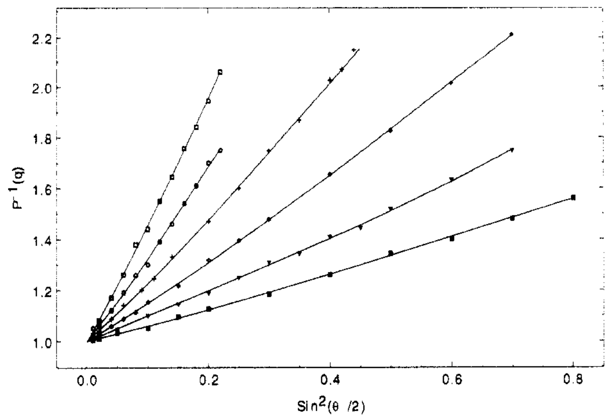

Figure 1. Angular dependence of scattering of light of NaPSS in NaCl solutions, extrapolated to zero polymer concentration, as a function of salt concentration. M_{NaCl} (M): (□) 0.001, (○) 0.004, (+) 0.01, (△) 0.05, (▼) 0.1, (■) 0.5.

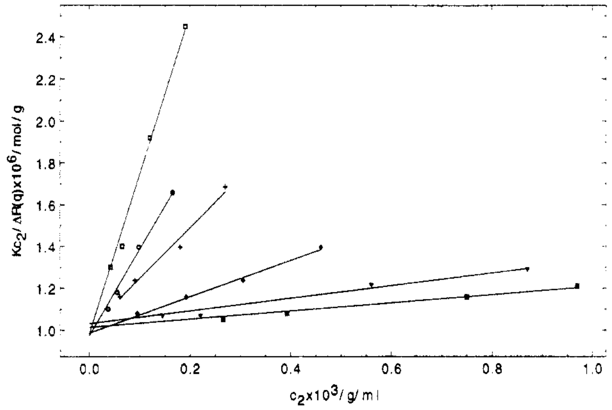

Figure 2. Concentration dependence of scattering of light of NaPSS in NaCl solutions, extrapolated to zero scattering angle. Symbols as in Figure 1.

Table 1. Solution Properties of NaPSS at Various NaCl Concentrations

NaCl (M)	$D_{20,\mathrm{sol}} \times 10^8$ (cm²/s)	$D_{20,\mathrm{w}} \times 10^8$ (cm²/s)	$S_{20,\mathrm{sol}}$ (S)	R_q (Å)	$A_2 \times 10^4$ (mL·mol/g²)	$M_{\mathrm{LS}} \times 10^{-5}$	$M_{\mathrm{SD}} \times 10^{-5}$
0.5	9.4	9.85	11.4	400	1.10	9.7	10.6
0.1	7.5	7.58	9.4	510	1.76	9.3	10.5
0.05	5.4	5.43		630	4.64	9.95	
0.01	4.2	4.20		780	11.50	9.95	
0.004	3.6	3.60		920	24.00	9.95	
0.001	3.2	3.20		1080	47.00	9.90	

IV. Results and Discussion

The angular dependence of scattering of light of NaPSS as a function of NaCl concentration is given in Figure 1, where $P(q)$ is the particle scattering factor equal to unity at $\theta = 0$.[17,47] Figure 2 gives the dependence of scattering on polyelectrolyte concentration. The basic equation for total intensity static scattering is[17,45,52]

$$Kc_2/\Delta R(q) = P^{-1}(q)\,M_2^{-1} + 2A_2c_2 + \ldots \qquad (3)$$

where K is a constant containing the square of the refractive index increment, $\Delta R(q)$ is the Rayleigh ratio proportional to the excess of solution over solvent scattering, M_2 is the polyelectrolyte molar mass, and A_2 is the second virial coefficient. The radius of gyration R_g is calculated from the curves in Figure 1 as described in Materials and Methods in the range $q^2R_g^{\,2} \leqslant 2$ or $P^{-1}(q) < 1.8$. The static and dynamic scattering and sedimentation results are summarized in Table 1 for all salt concentrations. The molar masses determined by total intensity light scattering

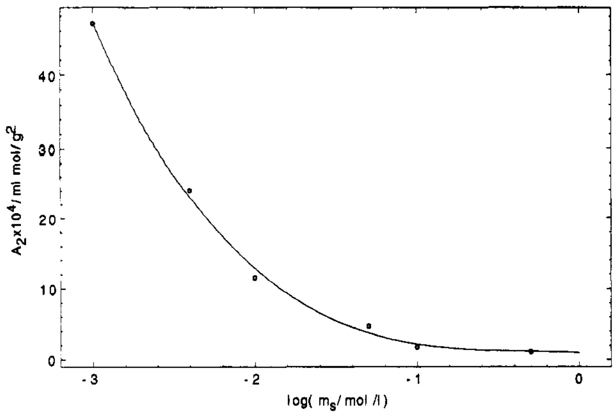

Figure 3. Second virial coefficient A_2 in NaPSS solutions as a function of NaCl concentration.

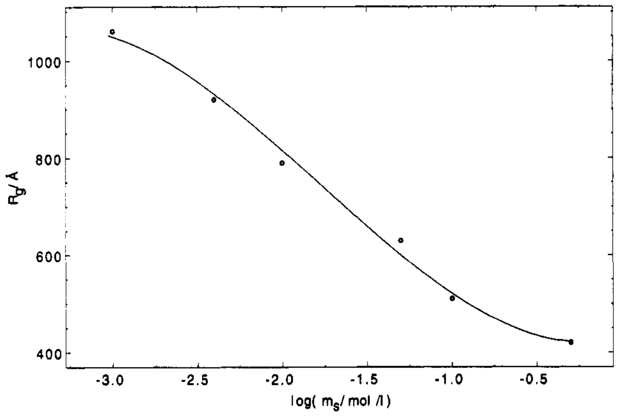

Figure 4. Radii of gyration R_g of NaPSS as a function of NaCl concentration.

Table 2. Calculation of Excluded-Volume Correction for NaPSS

NaCl (M)	α^a	α^b	α^c	$L_t^{a,d}$ (Å)	$L_t^{b,d}$ (Å)	$L_t^{c,d}$ (Å)	L_t^e (Å)
0.5	1.124	2.08	1.66	30.9	9.0	14.1	40.0
0.1	1.086	1.92	1.50	54.2	17.0	28.3	65.2
0.05	1.139	1.67	1.40	75.5	34.5	50.7	101.5
0.01	1.219	1.79	1.48	101.7	45.0	68.4	152.8
0.004	1.454	1.76	1.45	115.2	67.0	99.5	213.4
0.001	1.563	2.03	1.66	119.1	70.0	104.9	294.0

[a] Yamakawa–Tanaka procedure.[36,41] [b] Manning–Odijk procedure.[28,55] [c] Stigter[34] procedure. [d] Calculated from $R_{g0} = R_g/\alpha$ by the Benoit–Doty equation (see ref 36). For total length L we take 12380 Å, with 2.55 Å for the monomer (or charge) repeat distance. [e] Uncorrected for excluded volume.

(column 7) average to (9.80 ± 0.26) × 10^5 g/mol over all salt concentrations, confirming the validity of the linear concentration extrapolation. The Svedberg value[8,52] M_{sD} (column 8) is slightly higher (10.5 × 10^5 g/mol) but still within reasonable experimental range. The second virial coefficients A_2 (column 6 in Table 1 and Figure 3) and the radii of gyration R_g (column 5 in Table 1 and Figure 4) increase with decreasing salt concentration, yet even at the lowest salt concentration, 0.001 M NaCl, the value of R_g is far below the value $L/(12)^{1/2}$ which would correspond to that of a stretched rod, 3574 Å (see footnote *d* in Table 2). The dependence of the translational diffusion coefficient $D_{20,sol}$ on salt concentration is given in Figure 5.

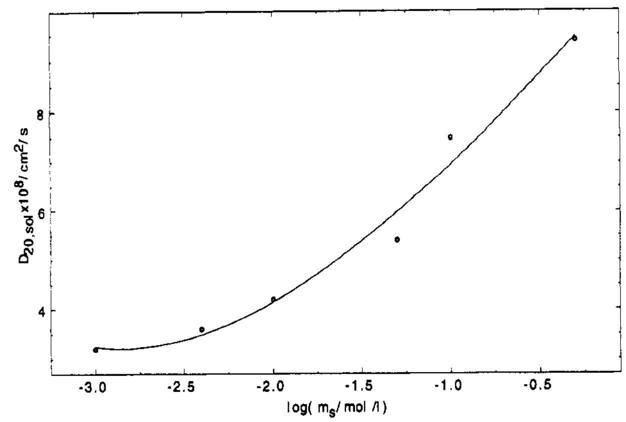

Figure 5. Diffusion coefficient $D_{20,sol}$ of NaPSS as a function of NaCl concentration.

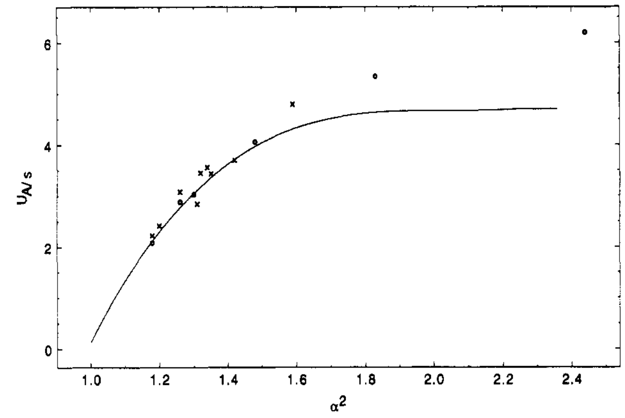

Figure 6. Universal plot $U_{A/s}$ vs expansion factor α^2 for DNA (×) and NaPSS (○). Solid curve is taken from Figure 12 of Oono.[53] DNA A_2 and R_g values have been smoothed from Figures 1 and 2 of ref 36.

The pattern of the dependence of the molecular parameters on salt concentration is interesting if combined in terms of the conformation-space renormalization-group approach,[53] which in the form given has not been extended to ionic systems. This may raise questions whether in excluded-volume calculations of polyelectrolyte systems the experimental value of A_2 may be used for the evaluation of both inter- and intramolecular excluded-volume interactions. The universal function[54]

$$U_{A/s} = A_2M^2/R_g^3N_{Av} \tag{4}$$

has been discussed by Oono[53] and is plotted in Figure 6 against the square of the excluded-volume expansion factor $\alpha = R_g/R_{g0}$. For polyelectrolytes the precise evaluation of α is problematic and we use here a procedure we have earlier used in the analysis of the dependence of DNA conformation on the concentration of salt[36] (see the discussion below). DNA is basically a very stiff chain with L_p = 285 Å,[35] whereas L_p = 14 Å for the much more flexible K- or NaPSS. (This value can be calculated from the experimental result R_g (Å) = $0.23M_2$ for KPSS in 3.1 M KCl at 25 °C in ref 39.) A similar value was obtained in ref 40. It is interesting that the Θ point for potassium poly(vinyl sulfonate),[27] a polyelectrolyte of similar charge density but without the aromatic benzene ring in the monomer unit, is at 0.65 M KCl at 25 °C. It is a striking result that both sets of data for NaPSS and DNA (Figure 6) superimpose and are in reasonable agreement with the calculated curve. Recalculation of our DNA data by Manning[55] and Monte Carlo and other calculations by Post[42] lead to considerably lower values of α in disagreement both with the Oono universal plot[53] and with excluded-volume calculations for NaPSS according to Odijk and Houwaert[28] and Stigter[33] to be discussed below.

An additional representation plots the universal ratio

$$U_{f/s} = f/\eta_0R_g \tag{5}$$

where the Stokes frictional coefficient f

$$f = 6\pi\eta_0 R_{\mathrm{H}} \qquad (6)$$

is obtained from the diffusion coefficient

$$D = kT/f \qquad (7)$$

In the universal plot of $U_{f/s}$ vs α^2 (Figure 7), the renormalization group theory value decreases to an asymptotic value of about 12. The NaPSS experimental values reach a value close to this, with some experimental scatter. An average value of $R_{\mathrm{H}}/R_{\mathrm{g}}$ is calculated by Akcasu and Ha[56] in Θ solvents to be 0.664 and in good solvents 0.537. We calculate for NaPSS an average of 0.601 ± 0.038 for all data. This is a good ballpark value in view of uncertainties associated with hydrodynamic data.

We conclude that our present NaPSS and the earlier DNA data[36] represent reliable experimental results of single-molecule behavior of two widely differing polyelectrolyte chains, allowing us to proceed to an examination of current excluded-volume and electrostatic expansion theories of polyelectrolyte systems.

V. Excluded Volume and Electrostatic Expansion

The electrostatic persistence length has been calculated by Odijk and Houwaert[28] and later by Le Bret[30] and Fixman[31] in two "state-of-the-art calculations" with nearly identical results. We have plotted in Figure 8 the theoretical curves of Le Bret as a function of salt concentration as evaluated by Fixman[31] with DNA charge parameters and by Tricot[29] with the corresponding parameters for NaPSS. The experimental data for DNA, not corrected for excluded volume,[36] are significantly higher than the theoretical curve. We have used $L_{\mathrm{p}} = 285$ Å[35] to evaluate L_{e} from the uncorrected values of L_{t} (Table 1 of ref 36). The corrections for excluded volume as summarized by Post[42] on the basis of an emotional interpretation by Manning[55] of existing theories, Monte Carlo calculations by Post,[42] and calculations according to Stigter[34] are not sufficient to bridge the gap and remain rather close to the uncorrected curve (Figure 8). In these calculations the value of the excluded-volume parameter α is considerably smaller than the value originally calculated by simple use[36] of the Yamakawa–Tanaka procedure. We note here that, if the use of the Yamakawa–Tanaka procedure is maintained,[36] then the introduction of the Yamakawa–Stockmayer[57] procedure for nonasymptotic chains affects the value of the excluded-volume parameter z but does not change the expansion factor α. The latter is changed by use of the Manning procedure[55] based on the excluded-volume calculation of Odijk.[28]

The values of L_{e} without excluded-volume correction for NaPSS calculated as before[36] for DNA by use of the Benoit–Doty equation[58] fall lower than the DNA values and rather close to the Le Bret theoretical curve. It should be noted, though, that both the DNA and NaPSS L_{e} values, representing a very stiff and an intrinsically flexible polyelectrolyte chain respectively, curve in the log–log plot (Figure 8) toward limiting values at very low salt concentrations, whereas the theoretical curves change curvature to increase in this range.

We have tried to correct the NaPSS data by the procedure suggested by Manning,[55] based on the Odijk and Houwaert[28] polyelectrolyte excluded-volume theory and the Yamakawa and Stockmayer[57] treatment of finite chains as well as by the Stigter[34] treatment which yielded close results in the case of DNA.[42] A summary of these calculations is given in Table 2.

It is seen here that unlike the above analysis, when applied to DNA, the excluded-volume corrections (footnotes b and c of Table 2) yield larger values of α, actually going through a minimum, than the Yamakawa–Tanaka correction (footnote a of Table 2), and the values of L_{t} are significantly decreased. Odijk and Houwaert[28] express many warnings concerning the limits of the validity of the excluded-volume calculation, predict a minimum and maximum for α as a function of salt concentration, and stipulate that the calculation is valid only when L_{e} is a "perturbation" of L_{p}. This may marginally apply in relation to the basically stiff DNA molecule ($L_{\mathrm{p}} = 285$ Å) yet certainly disqualifies application to the inherently flexible NaPSS molecule, with $L_{\mathrm{p}} = 14$ Å only. Use of alternate relations between α and z, as suggested by some authors,[37,57] is not likely to improve a basically flawed situation. Deeper insight must be gained to solve the polyelectrolyte excluded-volume problem. We would be happy for our DNA and NaPSS data to be tested by the authors[59,60] who claim to "provide the first rigorous treatment of the electrostatic excluded volume for a polyelectrolyte chain which incorporates the effect of salt concentration". In other recent contributions[61,62] the authors calculate "chain length dependence of the electrostatic persistence length L_{e} by numerical calculation" which "seems not to be confirmed by the experiments"! We are flooded by powerful calculating devices and exotic language loaned from modern physics, yet thinkers capable of the performance of Peter Debye seem to be sadly lacking.

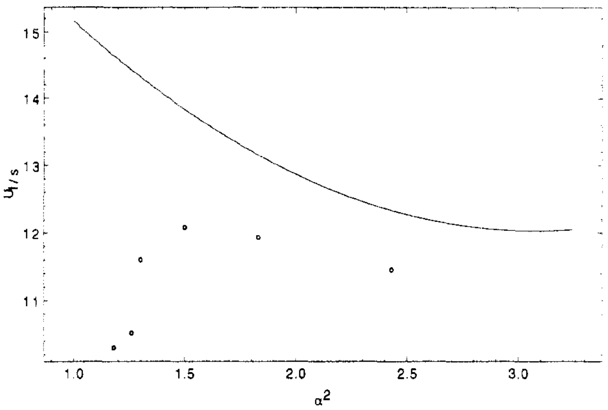

Figure 7. Universal plot $U_{f/s}$ vs expansion factor α^2 for NaPSS. The solid curve is taken from Figure 15 of Oono.[53]

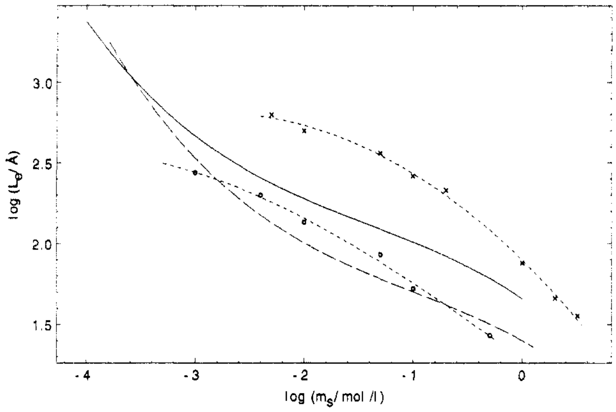

Figure 8. Electrostatic persistence length L_{e} of DNA and NaPSS as a function of salt concentration Le Bret[30] theoretical curves: (—) for DNA and (- -) NaPSS (cf. text). L_{e} values uncorrected for excluded volume: (×) DNA[35] using $L_{\mathrm{p}} = 285$ Å and (○) NaPSS, this work, using $L_{\mathrm{p}} = 14$ Å.

References and Notes

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