(8) Toporowski, P. M.; Roovers, J. *Macromolecules* **1978**, *11*, 365.
(9) Utiyama, H. In "Light Scattering from Polymer Solutions"; Hughes, M. B., Ed.; Academic Press: London, 1972.
(10) Roovers, J.; Toporowski, P. M. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1907.
(11) Benoit, H. *J. Polym. Sci.* **1953**, *11*, 507. Kolbovskii, Yu. Ya. *Polymer Sci. USSR (Engl. Transl.)* **1962**, *3*, 326.
(12) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.
(13) Bauer, B. J.; Hadjichristidis, N.; Fetters, L. J.; Roovers, J. *J. Am. Chem. Soc.* **1980**, *102*, 2410.
(14) Roovers, J., unpublished results.
(15) Roovers, J.; Bywater, S. *Macromolecules* **1972**, *5*, 384.
(16) Hadjichristidis, N.; Roovers, J. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 2521.
(17) Zilliox, J.-G. *Makromol. Chem.* **1972**, *156*, 121.
(18) Candau, F.; Rempp, P.; Benoit, H. *Macromolecules* **1972**, *5*, 627.
(19) McCrackin, F. L.; Mazur, J. *Macromolecules* **1981**, *14*, 1214.
(20) Daoud, M.; Cotton, J. P. *J. Phys.* **1982**, *43*, 531.
(21) McIntyre, D.; Mazur, J.; Wims, A. M. *J. Chem. Phys.* **1968**, *49*, 2887, 2896.
(22) Utiyama, H.; Tsunashima, Y.; Kurata, M. *J. Chem. Phys.* **1971**, *55*, 3133.
(23) Smith, T. E.; Carpenter, D. K. *Macromolecules* **1968**, *1*, 204.
(24) Mijnlieff, P. F.; Coumou, D. J.; Meisner, J. *J. Chem. Phys.* **1970**, *53*, 1775.
(25) Utiyama, H.; Utsumi, S.; Tsunashima, Y.; Kurata, M. *Macromolecules* **1978**, *11*, 506.
(26) Carpenter, D. K. *J. Chem. Phys.* **1972**, *56*, 1014.
(27) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(28) Stockmayer, W. H.; Fixman, M. *Ann. N.Y. Acad. Sci.* **1953**, *57*, 334.
(29) Mandelkern, L.; Flory, P. J. *J. Chem. Phys.* **1958**, *29*, 311.
(30) Berry, G. C. *J. Polym. Sci., Part A-2* **1968**, *6*, 1551.
(31) Zimm, B. H.; Kilb, R. W. *J. Polym. Sci.* **1959**, *37*, 19.
(32) Roovers, J. *Polymer* **1979**, *22*, 843.

Scaling Relations for Aqueous Polyelectrolyte–Salt Solutions. 1. Quasi-Elastic Light Scattering as a Function of Polyelectrolyte Concentration and Molar Mass

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ABSTRACT: Quasi-elastic light scattering experiments are reported on sodium poly(styrenesulfonate) solutions in aqueous 0.01 M NaCl. Samples of three different molar masses have been investigated as a function of the macromolecular concentration covering the dilute and the semidilute regimes. Experimental homodyne intensity autocorrelation functions of the scattered light were found to be nonexponential and had to be fitted with the help of a cumulant expansion using a floating value for the base line. From the value of the first cumulant an effective translational diffusion coefficient was evaluated. This diffusion coefficient exhibits a different behavior according to the concentration regime considered. In the dilute regime it is molar mass dependent but only slightly increases with concentration. In the semidilute regime the predictions of the scaling approach to the cooperative diffusion seem to be confirmed. The effective diffusion coefficient is molar mass independent and increases with concentration according to a power law that is close to the theoretically predicted one if adequate corrections for the change of the ionic strength of the solution with the polyelectrolyte concentration are applied. The experimentally found concentration power, larger than the theoretical value of 0.75, depends, however, on the value of the intrinsic persistence length of the polyelectrolyte (theoretically treated as a wormlike chain), which enters the correction factor mentioned. The results therefore seem to confirm that in the semidilute regime investigated a cooperative diffusion depending on the correlation length of the polyelectrolytes determines the diffusional effects as observed in quasi-elastic light scattering whereas in the dilute regime they depend on the translational behavior of individual chains. Both regimes are separated by a transition region where the effective diffusion coefficient seems to be molar mass and concentration dependent.

Introduction

Quasi-elastic light scattering provides a useful technique for determining the diffusion of macromolecules in solution. In the case of neutral polymers in good solvents it has been predicted that according to the concentration regime considered, different diffusion coefficients should be measured:[1] below a critical concentration c^*, which represents the concentration at which the individual chains in solution start to overlap considerably, the diffusion coefficient of the individual chains is measured. It is controlled by the averaged dimension of the macromolecular coils, for which the Flory limit of the radius of gyration may be taken as the characteristic quantity.[2] Above c^* intermolecular entanglements produce cooperative modes analogous to those of a permanent network. In the resulting cooperative diffusion the characteristic dimension is the correlation length ξ, which represents the average distance between successive entanglements along a chain and which should be independent of the molar mass of the chain but dependent on the concentration according to a $C^{-0.75}$ power law.[3] Several light scattering experiments have been reported in the literature[4-6] for solutions in the semidilute regime. In general, slightly different power dependences with concentration have been found as compared to the theoretical predictions.[7] In some studies also nonexponential behavior of the light scattering correlation function was reported, in contrast to the others.

More recently, Odijk[8] has extended the scaling relation for neutral polymers to the case of semidilute polyelectrolyte solutions with or without added salt. In this approach changes in the flexibility of the macromolecular chain due to charge interactions are taken into account within the context of a wormlike chain model.[9] In the presence of an excess of the added salt the theory predicts behavior of the polyelectrolytes analogous to that of neutral polymers if the necessary corrections for charge interactions are applied. In an earlier short communication we found some confirmation of the theoretical prediction

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concerning the concentration dependence of the diffusion coefficient in the semidilute regime for sodium poly(styrenesulfonate) (NaPSS) in 0.01 M NaCl solutions.[10] Here we report a more detailed investigation of several NaPSS systems, which have been studied in order to verify the proposed scaling relation. Not only the concentration power law of the diffusion coefficient in the semidilute regime but also its molar mass independence will be checked experimentally.

Theory

Quasi-elastic light scattering experiments probe local concentration fluctuations in solution.[11] The quantity of interest is the structure factor defined by

$$S(\mathbf{q},t) = \langle \delta c(\mathbf{q},t) \delta c^*(\mathbf{q},0) \rangle \tag{1}$$

This structure factor represents the time-dependent correlation function of the spatial Fourier transform $\delta c(\mathbf{q},t)$ of the local concentration fluctuations at time t and for scattering vector $\mathbf{q}$ of the scattered light (with δc^* its complex conjugate). For a system of noninteracting, identical, isotropic particles small compared to the wavelength of the light, it can be shown that the structure factor simplifies to an exponential expression.

$$S(\mathbf{q},t) = S(\mathbf{q},0) \exp(-D_{\mathrm{T}} q^2 t) \tag{2}$$

Here, D_{T} stands for the translational diffusion coefficient of the isotropic particle and q is the length of the scattering vector

$$q = (4\pi n_{\mathrm{s}}/\lambda_{\mathrm{v}}) \sin (\theta/2) \tag{3}$$

with λ_{v} the wavelength in vacuo of the incident light, n_{s} the refractive index of the solution, and θ the scattering angle.

According to de Gennes[3] the dynamical behavior of isolated polymer coils strongly resembles the dynamical behavior of (hard) spherical particles. Quasi-elastic light scattering performed at very low polymer concentrations should give information about the translational diffusion coefficient of the individual coils. Assuming that the Stokes–Einstein relation holds, the following expression for the diffusion coefficient will be applicable:

$$D_{\mathrm{T}} = k_{\mathrm{B}}T/6\pi\eta R_{\mathrm{H}} \tag{4}$$

Here, R_{H} is the hydrodynamic radius of the polymer coil and η the viscosity of the solvent. In general, R_{H} may differ from the mean geometrical size of an isolated chain as given by the radius of gyration $\langle S^2 \rangle^{1/2}$. Even in the dilute regime a concentration effect is to be expected but of small magnitude due to the interaction between the spherical particles.[12]

In the semidilute regime the interactions increase significantly and the coils are assumed to interpenetrate. The fluctuations probed by light scattering are due to cooperative modes of the strongly entangled chains, for which the correlation length ξ is the essential length scale, inter alia, insofar as the relaxation of the fluctuations is concerned. Here de Gennes assumes that each chain can be pictured as a collection of uncorrelated "blobs" with average dimension ξ and that the correlation time of the cooperative modes in semidilute dynamical networks can be described in terms of the diffusion of individual "blobs". Therefore for $c \gg c^*$ the following relations are expected:

$$S(\mathbf{q},t) = S(\mathbf{q},0) \exp(-D_{\mathrm{c}} q^2 t) \tag{5}$$

$$D_{\mathrm{c}} = k_{\mathrm{B}}T/6\pi\eta\xi \tag{6}$$

The mutual diffusion coefficient D_{c} has been considered as the Einstein diffusion coefficient of an individual "blob". The factor 6π has no physical significance, however, and has only been introduced to maintain the similarity between (6) and (4). Note that the simple relation between D_{c} and ξ can only hold if the chain is extremely long ($l \gg \xi$, where l is the contour length of the polymer) and if the time scale of the mutual diffusion process is much smaller than that of reptation.

Odijk has argued[8] that analogous relations should hold in the case of polyelectrolyte solutions in the presence of an excess of added salt (here assumed to be mono-monovalent) provided that the polyelectrolyte chain can be represented as a wormlike chain with a persistence length L_{t}, consisting of a structural or intrinsic part L_{p} (corresponding to the persistence length of the uncharged polymer) and an electrostatic part L_{e} arising from the screened charge interactions along the chain, which increase its stiffness. Assuming that for the interactions between two charges fixed on a given polyelectrolyte the potential of mean force is given by a Debye–Hückel potential with screening length κ^{-1} defined by

$$\kappa^2 = 8\pi Q\mu \tag{7}$$

where μ is the ionic strength of the solution, $Q = q^2/Dk_{\mathrm{B}}T$ is the Bjerrum length, q is the elementary charge, and D is the relative permittivity of the solvent, the following expression was derived for L_{t}:[9]

$$L_{\mathrm{t}} = L_{\mathrm{p}} + (Q/4\kappa^2 A^2)f = L_{\mathrm{p}} + L_{\mathrm{e}} \tag{8}$$

Here, A is the average contour distance between two successive charges on the chain; if the chain carries Z elementary charges distributed uniformly along the chain, $A = l/Z$ so that A is inversely proportional to the linear charge density of the chain. The factor f has been introduced here in order to account for the effective charge of the polyelectrolyte chain, which may be reduced due to strong interactions with the counterions. According to the simple "condensation theory",[13,14] the effective charge Z_{eff} of the polyion is only reduced with respect to Z for $A < Q$; then $f = 1$ for $A > Q$ and $f = A^2/Q^2$ for $A < Q$. In the latter case L_{e} in (8) becomes independent of the linear charge density of the chain. Equation 8 is a first approximation that should hold if the following conditions are obeyed: $A \ll \kappa^{-1}$ and $L_{\mathrm{t}} \gg \kappa^{-1}$.

The following expressions may be derived for the crossover concentration c^* and for the concentration dependence of the correlation length ξ in the case of polyelectrolyte solutions with an excess of salt (all concentrations expressed in monomeric units per unit volume):

$$c^* \simeq N R_{\mathrm{F}}^{-3} \simeq a^{-1} l^{-4/5} (L_{\mathrm{t}}/\kappa)^{-3/5} \tag{9}$$

$$\xi \simeq R_{\mathrm{F}}(c/c^*)^{3/4} \simeq (L_{\mathrm{t}}/\kappa)^{-1/4} (ac)^{-3/4} \qquad c \gg c^* \tag{10}$$

Here, R_{F} is the Flory limit of the radius of gyration, which can reasonably be approximated by the following expression:[8]

$$R_{\mathrm{F}} \simeq l^{3/5} (L_{\mathrm{t}}/\kappa)^{1/5} \tag{11}$$

a is the length of a monomeric unit defined through the relation $l = ZA = Na$, with N the number of monomeric units per chain. Thus $a = (Z/N)A = \alpha A$, where α is the average degree of charge. In the particular case where each monomeric unit carries an elementary charge, as assumed for the polyelectrolytes investigated here, we have $Z = N$ and $a = A$.

As (in the presence of an excess of salt) L_{t} and κ are independent of $l \sim N$, the dependence of c^* on l, according to (9), is the same as for neutral polymers. The influence of the screened charge interactions appears through the factor $(L_{\mathrm{t}}/\kappa)^{-3/5}$.

Equation 10 predicts in the semidilute concentration regime a decrease of the correlation length with concentration according to the power law $c^{-3/4}$, provided that α and L_t/κ remain constant.

According to (6) and (10) it is to be expected that the mutual diffusion coefficient D_c as measured in the semidilute regime of polyelectrolyte solutions in the presence of an excess of salt will be molar mass independent and will increase with concentration according to a power law $c^{3/4}$.

Materials and Methods

The sodium salt of poly(styrenesulfonate) (NaPSS) was purchased from Pressure Chemical Co. Three different samples were used with molar masses of 4×10^5, 6.5×10^5, and 12×10^5 g mol^{-1}. These samples were prepared by sulfonation of well-defined, nearly monodisperse samples of polystyrene. According to the manufacturer the polyelectrolytes are characterized by $M_w/M_n < 1.1$. Our own determinations have shown that the degree of sulfonation is close to unity, in contrast to the manufacturer's specifications.

The concentration dependence of the diffusion coefficient of solutions of the three samples in 0.01 M NaCl was investigated. All solutions were prepared with deionized water and NaCl of analytical grade (Merck); they were made dust-free by filtration through 0.22-μm Millipore filters. The concentration of NaPSS in solution was always determined spectrophotometrically at 261 nm after filtration. The value of the extinction coefficient at this wavelength was established by calibration with Beer's law, with corrections for the water content of the NaPSS, as determined by IR, applied.

Quasi-elastic light scattering measurements were performed with the help of a Malvern 4300 photocorrelation spectrometer incorporating a Type K7023/2 cm 96 (96 channels) Malvern digital correlator. The light source was a Spectra Physics Type 165 argon ion laser operating at 514.5 nm. Optically cylindrical cells for these measurements were made by Telescope b.v., Delft. Intensity correlation functions were determined at the constant temperature of 25 °C and at several scattering angles between 30 and 90° (generally at 30, 37.5, 45, 60, 75, and 90°). The lower limit of the scattering angle was chosen such that heterodyne contributions to the measured correlation function can be neglected.

For each solution the buildup of the correlation function was followed on the scope of the correlator and recorded finally on paper tape (using a Facit paper tape puncher).

Data Analysis

From the experiments a normalized correlation function $Y(\tau)$ can be obtained, which is closely related to the normalized intensity correlation function $g^{(2)}(\tau)$. If it may be assumed that the scattered field has Gaussian statistics, the latter may be expressed as a function of the normalized field correlation function $g^{(1)}(\tau)$, itself proportional to the structure factor as given by (1), through the Siegert relation.

$$g^{(2)}(\tau) = 1 + |g^{(1)}(\tau)|^2 = 1 + e^{-2D_T q^2 \tau} \qquad (12)$$

In the last member of (12) the structure factor has been represented by its general form (2). For a system of identical, noninteracting particles, $Y(\tau)$ may then be represented by

$$Y(\tau) = 1 + Ae^{-2\Gamma\tau} \qquad (13)$$

where the decay or relaxation rate Γ is related to D_T by

$$\Gamma(q) = D_T q^2 \qquad (14)$$

The factor A in (13) takes into account nonideal behavior of the experimental setup such as incomplete spatial coherence, detector dark current, etc. The function $Y(\tau)$ should reach the theoretical base line value of unity for large values of τ. Spurious scattering by dust and other sources of parasitic scattering are responsible for the experimental observation that the base line will deviate from its theoretical value. Several authors[15-17] in trying to fit experimental results to an analytical expression for Y have pointed out that the use of an additional fit parameter A' for the base line yields better reproducible results with lower standard deviations in the parameter values, as misnormalization of the data may be corrected in this way.

$$Y(\tau) = A' + Ae^{-2\Gamma\tau} \qquad (15)$$

It is often found that the experimental correlation function does not behave as a single exponential such as (15). There may be many causes responsible for such a behavior, all originating in deviations from the different conditions that must be met in order that (2) should hold. It is, in general, difficult to establish which of these causes is primarily responsible for the nonexponential time dependence of $Y(\tau)$. For heterodisperse macromolecular systems a cumulant expansion for the electric field correlation function has been proposed[18] but more recently, it has been suggested that such an expansion could also be used for systems where the nonexponential behavior of $Y(\tau)$ is mainly due to hydrodynamic or electrostatic interactions and to contributions of charge fluctuations.[19-21] Therefore in our data analysis we have used either (15) or its generalization through a cumulant expansion

$$Y(\tau) = A' + A \exp\left\{-2K_1\tau + \frac{2K_2}{2!K_1^2}(K_1\tau)^2 - \frac{2K_3}{3!K_1^3}(K_1\tau)^3 + ...\right\} \qquad (16)$$

where K_i represents the ith cumulant. Both Γ or the cumulants and the additional parameters A and A' could be obtained by fitting experimental values of $Y(\tau)$ of a given experiment to (15) and (16) by a nonlinear least-squares technique using the Gauss–Newton algorithm.[22]

Three criteria were used to conclude that a fit is satisfactory:

(1) The fitted base line A should not differ from the theoretical value unity by more than 0.5%.

(2) If the quality factor QF of the fit is defined by

$$\mathrm{QF} = 1 - \frac{\sum_{i=1}^{N-1} (y_i - \tilde{y}_i)(y_{i+1} - \tilde{y}_{i+1})}{\sum_{i=1}^{N-1} (y_i - \tilde{y}_i)^2} \qquad (17)$$

where y_i is the value of the ith experimental point, $\tilde{y}_i$ its value according to the fitted curve, and N the total number of points on a curve ($N < 96$), QF should not be smaller than 0.7.

(3) The standard deviations in the fit value of the parameters must be reasonable as compared to what is accepted in recent literature. This means that the standard deviation in the first cumulant K_1 or the decay rate for a single-exponential fit should be of the order 1% or smaller, for K_2/K_1^2, a value of 10–30% would be tolerable, etc.

When (16) is used, the first cumulant K_1 may considered to be related to an effective diffusion coefficient D_{eff} if it is linearly dependent on q^2.

$$K_1 = D_{\mathrm{eff}} q^2 \qquad (18)$$

This is expected to hold in systems where no local ordering occurs as revealed by a static structure factor $S(\mathbf{q},0)$ equal to unity.[3] The normalized second cumulant (K_2/K_1^2) may be considered as an estimate for the deviation from single exponentiality of the correlation function $Y(\tau)$ (provided the series in the exponent converges rapidly).

As has been reported previously[10] NaPSS in 0.01 M NaCl solution does not yield measured correlation func-

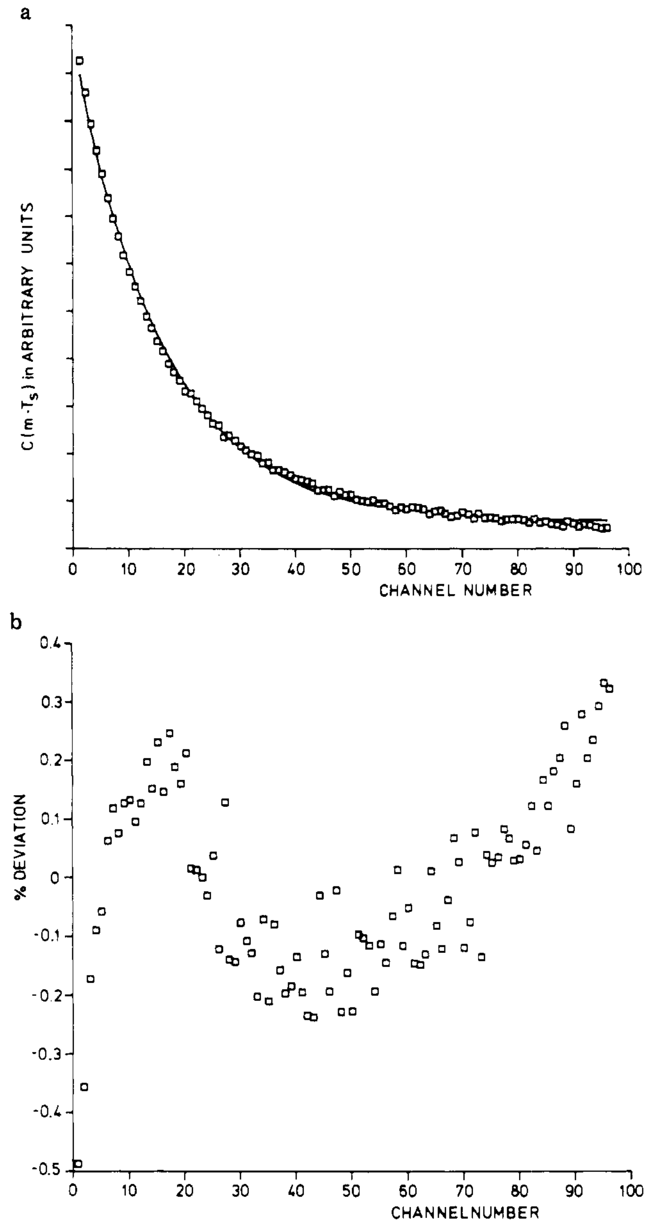

Figure 1. Experimental data of the intensity correlation function for 6.98 g L^{-1} NaPSS ($M_w = 6.5 \times 10^5$ g mol^{-1}) in 0.01 M NaCl at 25 °C at an angle of 37.5°: (a) data fitted to a single-exponential function; (b) deviation of experimental points with respect to fitted curve.

tions of the simple exponential type. This has been confirmed for all the solutions studied in the present investigation. In Figure 1a an example is shown of the fit of experimental points $Y(\tau)$ to an exponential function (15). The fit is of poor quality as is even more strikingly demonstrated in Figure 1b. In the latter the deviation between experimental points and calculated values according to the fitted function is plotted against τ. The figure exhibits a "structural" behavior, representative of a poor fit. For fits to a single exponential the QF values are, moreover, of the order 0.2–0.3 in all cases.

The same data fitted to the cumulant expression (16) with three moments (five parameters) are presented in Figure 2a. Together with the plot of the deviations as functions of τ (Figure 2b) it demonstrates the superior quality of the cumulant fit. Typical values for the normalized second cumulant are of the order 0.3, with no significant variation on polyelectrolyte concentration or molar mass. Under the present circumstances this means that the deviation of $Y(\tau)$ from a single-exponential function is very small in absolute value (compare also Figure 1b). Unfortunately, the deviations are significant and systematic and cannot be neglected.

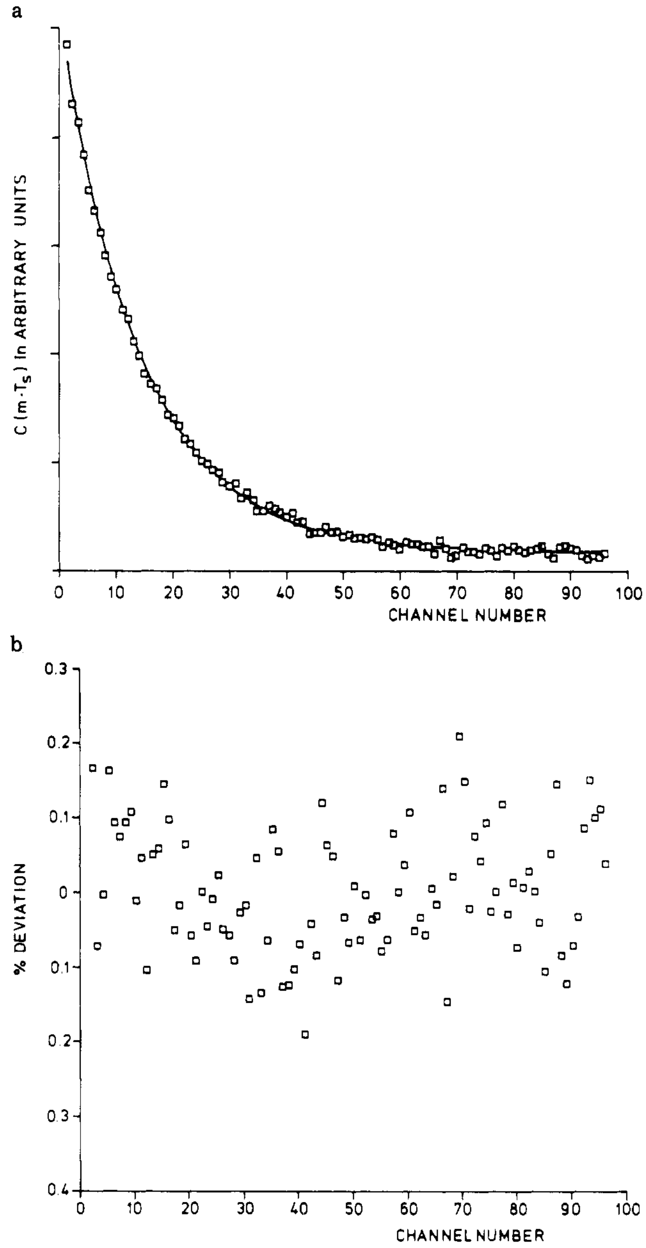

Figure 2. Same data as in Figure 1: (a) fitted to cumulant expression 16 with five parameters; (b) deviation of experimental points with respect to fitted curve.

There is yet another, empirical reason to prefer the cumulant expression over the single-exponential function as a representation for $Y(\tau)$. It is found that the values of K_1 yield a better linear fit to $\sin^2(\theta/2)$ than the values of the relaxation rate Γ obtained from the single exponential (see Figure 3). Moreover, the reproducibility of K_1 is better than that of Γ. It is interesting to note that, given an experimental $Y(\tau)$, we have always found the order of magnitude of K_1 and Γ to be the same; in fact, the value of Γ is 10–12% smaller than the corresponding value of K_1, independent of the system considered. Furthermore, applying the procedure suggested by Brown et al.,[21] we find that for the different NaPSS solutions investigated the values of K_1 and K_2/K_1^2 are *insensitive* to the choice of sampling time (see Figure 4).

As pointed out before there may be several reasons why $Y(\tau)$ deviates from an exponential function. The origin of the observed deviations is, however, difficult to trace,

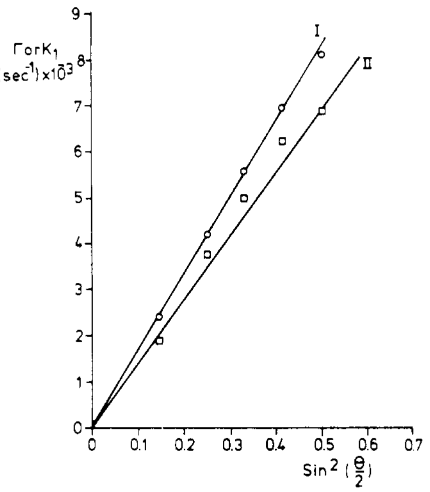

Figure 3. Comparison of the $\sin^2(\theta/2)$ dependence of the relaxation ratio Γ (□) and the first cumulant K_1 (○) obtained by single exponential (II) and a cumulant expansion (I) fit for NaPSS in 0.01 M NaCl at 25 °C ($M_w = 4 \times 10^5$ g mol^{-1}), $C = 0.6$ g L^{-1}, and $45 < \theta < 90°$).

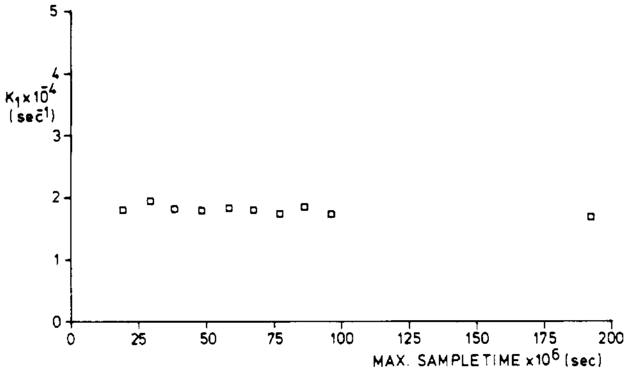

Figure 4. Dependence of the first cumulant on the sampling time for 6.98 g L^{-1} NaPSS ($M_w = 6.5 \times 10^5$ g mol^{-1}), in 0.01 M NaCl at 25 °C from measurements at $\theta = 45°$.

particularly in view of the insensitivity of the higher order cumulants to experimental conditions. These deviations are not artifacts traceable to the experimental setup, however. We have found that for the parent polystyrene of one of the NaPSS samples used, the measured correlation function in toluene solution can be fitted satisfactorily to a single-exponential function. Furthermore, the relaxation rate Γ thus found follows closely the square law of the scattering angle. Finally, the method of Brown et al.[21] yields values for the second cumulant that are zero within the uncertainty of the data, independent of the sampling time used. For this polystyrene $Y(\tau)$ can well be fitted to an exponential correlation function and therefore no systematic deviations originating in the experimental setup are apparent. It is not evident, however, that for the same reasons molar mass heterodispersity can be ruled out as the origin for the deviation of $Y(\tau)$ from a single-exponential function in the case of NaPSS. The samples of PSS have been prepared by sulfonation of the parent polystyrene and even for a degree of sulfonation close to unity some heterodispersity cannot be excluded. We shall not pursue here a discussion of the physical meaning of the second (or higher order) cumulant also in view of the uncertainty introduced by the use of a floating base line. The effective diffusion coefficients D_{eff} for the different systems investigated have been obtained from the slope of the linear dependence of K_1 (derived from a five-parameter cumulant expansion (fit) on $\sin^2(\theta/2)$.

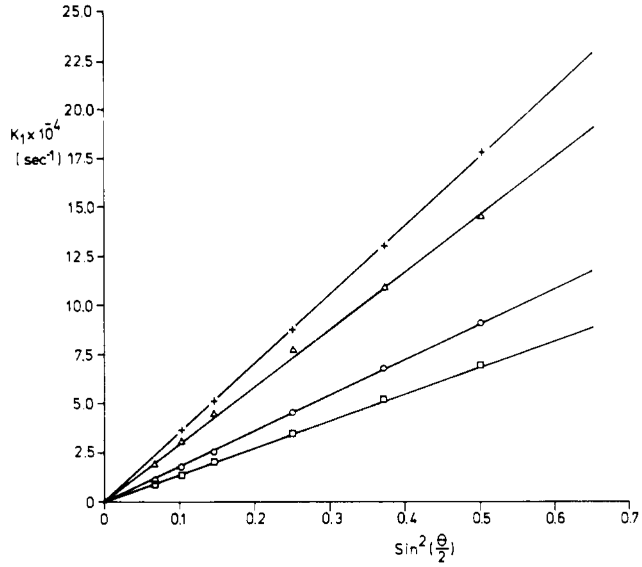

Figure 5. $\sin^2(\theta/2)$ dependence of the first cumulant of the intensity correlation function of NaPSS in 0.01 M NaCl at 25 °C in the semidilute concentration regime ($M_w = 6.5 \times 10^5$ g mol^{-1}; C = 6.98 (□), 9.6 (○), 19.6 (△), and 26.4 g L^{-1} (+)).

Table I
Effective Diffusion Coefficient D_{eff} of NaPSS in 0.01 M NaCl at 25 °C: $M_w = 4 \times 10^5$ g mol^{-1}, $L_p = 10^{-7}$ cm, $C^* = 2.5$ g L^{-1}

C, g L^{-1}	$10^8 D_{\text{eff}}$, cm^2 s^{-1}	$10^3 B$, cm$^{3/2}$ s^{-1}
0.01	9.09	
0.30	10.1	
0.64	15.8	
1.44	33.8	
3.26	54.0	
5.1	87.1	
12.1	199	4.07
13.0	198	4.07
16.0	239	5.13
17.5	247	5.25

Table II
Effective Diffusion Coefficient D_{eff} of NaPSS in 0.01 M NaCl at 25 °C: $M_w = 6.5 \times 10^5$ g mol^{-1}, $L_p = 10^{-7}$ cm, and $C^* = 1.38$ g L^{-1}

C, g L^{-1}	$10^8 D_{\text{eff}}$, cm^2 s^{-1}	$10^3 B$, cm$^{3/2}$ s^{-1}
0.049	7.27	
0.282	7.46	
0.802	12.8	
4.22	71.3	
6.98	130	2.48
9.65	171	3.40
16.2	246	5.27
19.6	277	6.12
26.4	333	7.74

Results and Discussion

For each molar mass of NaPSS several solutions of different polymer concentration C (in g L^{-1}) in 0.01 M NaCl have been studied. Conditions were chosen in such a way that a few concentrations at least could be assumed to be well below C^* as calculated according to (9). In Figure 5 an example of the dependence of K_1 on the scattering angle for some semidilute systems is shown and in Figure 6 for some dilute ones. Experimental results transformed into D_{eff} as explained above are collected in Tables I-III.

From Figure 5 it can be concluded that K_1 for the semidilute solutions follows closely the relation (18). For the

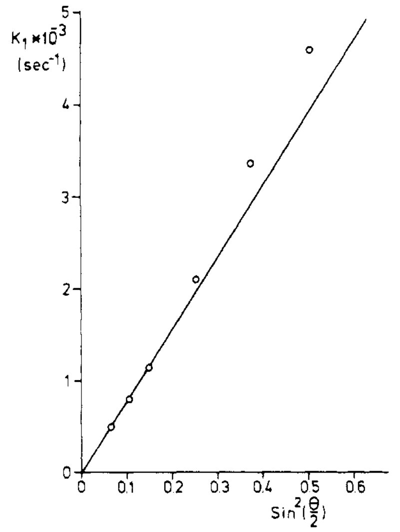

Figure 6. $\sin^2(\theta/2)$ dependence of the first cumulant for NaPSS in 0.01 M NaCl in the dilute concentration region ($M_w = 6.5 \times 10^5$ g mol^{-1}, $C = 0.28$ g L^{-1}).

Table III
Effective Diffusion Coefficient D_{eff} of NaPSS in 0.01 M NaCl at 25 °C: $M_w = 12 \times 10^5$ g mol^{-1}, $L_p = 10^{-7}$ cm, and $C^* = 0.85$ g L^{-1}

C, g L^{-1}	$10^8 D_{\mathrm{eff}}$, cm^2 s^{-1}	$10^3 B$, cm$^{3/2}$ s^{-1}
0.01	4.10	
0.05	4.20	
0.18	6.30	
0.42	9.20	
2.36	45.9	
4.20	96.7	1.78
6.01	124	2.34
8.30	153	3.02
10.7	202	4.07
20.6	277	6.16
23.5	307	7.08
27.0	323	7.56

dilute systems, especially at the lowest concentrations, a departure of the square-law dependence occurs for angles larger than 60° ($\sin^2(\theta/2) > 0.25$). A possible reason for such deviations is a contribution from the internal relaxation of the coils to the measured total relaxation of the concentration fluctuations. Note that for the lower concentrations in the dilute regime, the average dimensions of a single chain ($\sim R_F$) will already be of the order of q^{-1} for the higher scattering angles. Therefore for the dilute systems we have used the initial slope of K_1 vs. $\sin^2(\theta/2)$ for $\theta < 60°$.

As can be seen from Figure 7, where the results of Tables I–III have plotted as $\log D_{\mathrm{eff}}$ vs. $\log C$, three different concentration regions may be distinguished. At $C \ll C^*$ the diffusion coefficients change only very slightly with C, in qualitative agreement with the theoretical predictions for very dilute solutions. At the other end ($C \gg C^*$) an important increase of D_{eff} with C is observed, nearly independent of the molar mass, which also seems to confirm the predictions of scaling theory. In between these two a transition region is observed where D_{eff} starts to increase considerably but larger differences between the behavior of polyions with different molar masses are observed.

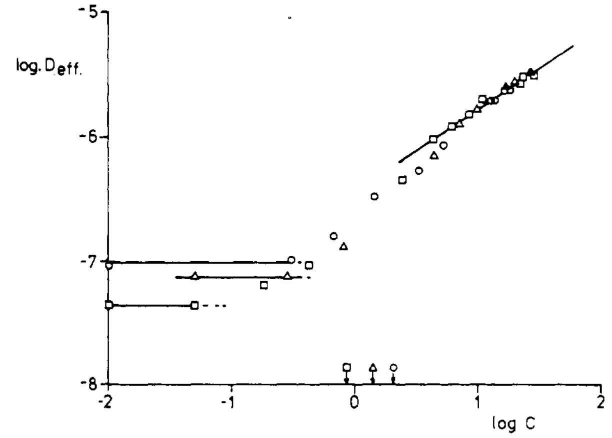

Figure 7. $\log D_{\mathrm{eff}}$ vs. $\log C$ for NaPSS in 0.01 M NaCl at 25 °C ($M_w = 4 \times 10^5$ (○), 6.5×10^5 (△), and 12×10^5 g mol^{-1} (□)). The arrows indicate the location of the theoretical values of $\log C^*$.

In order to check scaling theory more quantitatively, implying $D_{\mathrm{eff}} \sim \xi^{-1}$, we have to compare the observed concentration dependence of D_{eff} in the semidilute concentration regime to the theoretical prediction as given by (10). In fact, $\log D_{\mathrm{eff}}$ can be represented as a linear function of $\log C$, considering all experimental results for which $C > 3C^*$ (16 in total; see Figure 7). A least-squares fit yields $\log D_{\mathrm{eff}} = (6.42 \pm 0.2) + (0.66 \pm 0.02) \log C$ with a standard deviation of 0.02. Here, the slope is definitely smaller than the predicted value 0.75. By testing (10) in this way we have implicitly assumed that $(\kappa/L_t)^{1/4}$ is concentration independent, an assumption that will be fulfilled if there is a large excess of low molar mass electrolyte. In the present case, however, the salt concentration is rather low (0.01 M) and the polyelectrolyte concentration reaches relatively high values. Therefore the cations from the polyelectrolyte may also contribute to the ionic strength, which determines κ and also L_e, and thus $(\kappa/L_t)^{1/4}$ no longer will be independent of C.

Correction for this effect implies further assumptions. Empirical evidence shows that due to strong interactions between counterions and polyions a certain portion of the former will be thermodynamically "inactive". Thus the following definition of the ionic strength may be used:

$$\mu = \tfrac{1}{2}[2c_s + Z_{\mathrm{eff}} c_M](10^{-3} N_A) = c_s\left[1 + \left(\frac{Z^*}{Z}\right)\alpha \frac{c}{2c_s}\right](10^{-3} N_A) \quad (19)$$

Here, c_s is the molar salt concentration, c_M is the concentration of polyions in mol L^{-1}, $c = Nc_M$ (the latter in mononomol L^{-1}), N_A is Avogadro's constant, and Z and Z^* stand for the real number of elementary charges and the "effective" number, respectively, borne by the polyions. An estimate for Z^*/Z may be found from condensation theory, which predicts for $A < Q$

$$\frac{Z^*}{Z} = \lambda^{-1} \equiv \frac{A}{Q} = \frac{a}{Q\alpha} \qquad \lambda > 1 \quad (20)$$

Combining (19) and (20), one obtains

$$\mu = c_s\left[1 + \left(\frac{a}{Q}\right)\frac{c}{2c_s}\right](10^{-3} N_A) \quad (21)$$

so that μ will be an increasing function of C. For NaPSS, if the degree of sulfonation is larger than 0.36, which is certainly the case for the samples in this investigation, the condition $\lambda > 1$ is fulfilled ($a \simeq 2.5 \times 10^{-8}$ cm; $Q \simeq 7 \times 10^{-8}$ cm). Thus (21) may be used to estimate κ and L_e, for the latter assuming consistently $f = A^2/Q^2$. Both quantities will depend on C.

In order to check the validity of (10) it may therefore be more reliable to look at the concentration dependence of the auxiliary quantity B.

$$B \equiv D_{\mathrm{eff}}(\kappa/L_t)^{1/4} \quad (22)$$

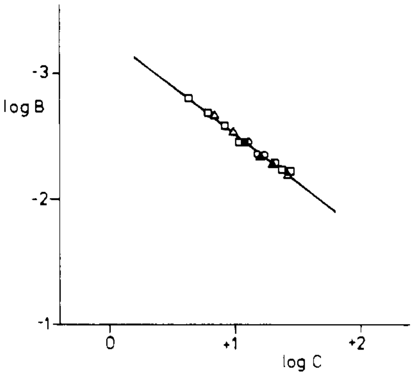

Figure 8. Data of $B \equiv D_{\mathrm{eff}}(\kappa/L_t)^{1/4}$ vs. log C. Full drawn curve is a least-squares fit. Here, $L_p = 3 \times 10^{-7}$ cm.

instead of D_{eff} itself. According to (10), B should be proportional to $C^{3/4}$ under all conditions in the semidilute region. A difficulty arises, however, as in order to calculate L_t the value of the intrinsic part of the persistence length L_p must be known. It turns out that log B depends linearly on log C (see Figure 8) but that the power law for B depends sensibly on the choice for the value of L_p, as shown in the following results obtained from a linear least-squares fit using the experimental values of D_{eff}:

$$\log B = -(3.26 \pm 0.02) + (0.80 \pm 0.02) \log C \qquad L_p = 10 \times 10^{-8} \text{ cm}$$

$$\log B = -(3.28 \pm 0.02) + (0.77 \pm 0.02) \log C \qquad L_p = 30 \times 10^{-8} \text{ cm}$$

$$\log B = -(3.30 \pm 0.02) + (0.76 \pm 0.02) \log C \qquad L_p = 50 \times 10^{-8} \text{ cm}$$

For the three cases quoted, the standard deviation in the fit is 0.020, 0.017, and 0.016, respectively. The value of L_p for poly(styrenesulfonate) chains has not yet been determined accurately although the value $L_p = 10 \times 10^{-8}$ cm has been suggested.[23] In view of the bulky SO_3 group fixed on the phenyl rings, a larger value is not impossible. It is too speculative, however, to conclude that L_p would be nearer 50×10^{-8} cm because this yields the correct power law as predicted theoretically. It is not uncommon to find small discrepancies between experimental and theoretical exponents when testing scaling law.[7] Also from light scattering experiments on semidilute solutions of neutral macromolecules slightly different powers than 0.75 have been found for the concentration dependence.[4-6] On the other hand, the experimental conditions are not ideal for testing (10), as the theory has been developed for the case of an excess of low molar mass electrolyte such that $L_t \gg \kappa^{-1}$ holds. Although for all the systems investigated $L_t > \kappa^{-1}$, both quantities are of the same order of magnitude, particularly if L_p is assumed to be close to 50×10^{-8} cm. Finally, the expression of μ as well as that of L_e involves a certain number of assumptions as well as the repeated use of the simple condensation approach, which is known to be only semiquantitatively correct.

Table IV
Comparison of the Hydrodynamic Radius Calculated from D_{eff}^0 with the Flory Radius and Root-Mean-Square Radius of Gyration[a]

$10^{-5}M_w$, g mol^{-1}	$10^8 D_{\mathrm{eff}}^0$, cm^2 s^{-1}	$10^8 R_H$, cm	$10^8 R_F$, cm	$10^8 \langle S^2\rangle^{1/2}$, cm
4	9.0	270	620	450
6.5	7.5	323	920	600
12	4.0	606	1330	860

[a] $a = 2.5 \times 10^{-8}$ cm, $L_p = 10^{-7}$ cm, $M_m = 206$ g mol^{-1}, and $\lambda > 1$. D_{eff}^0 is D_{eff} at the lowest concentration investigated; $\langle S^2\rangle^{1/2}$ is calculated according to eq 24–27.

It is interesting to note that the factor in front of the concentration dependence of B is of the right order of magnitude according to the theoretical predictions. Combining (6), (10), and (22), we find the theoretical expression

$$B \simeq \frac{k_B}{\phi\eta}\left[\frac{aN_A}{1000M_m}\right]^{\nu} C^{\nu} \tag{23}$$

where C is expressed in g L^{-1}, M_m is the molar mass of a monomeric unit (206 g mol^{-1} for sodium styrenesulfonate), and ϕ is a numerical constant analogous to the dubious 6π in (6). In water at 298 K ($\eta = 0.009$ P) the factor in front of C^{ν} is given by the following values (depending on the choice of ν):

$$B/C^{\nu} = 2.2 \times 10^{-3}/\phi \qquad \nu = 0.80$$

$$B/C^{\nu} = 1.1 \times 10^{-3}/\phi \qquad \nu = 0.77$$

$$B/C^{\nu} = 0.8 \times 10^{-3}/\phi \qquad \nu = 0.76$$

to be compared to the fitted value, which is of the order 5×10^{-4}. This would suggest that $\phi < 6$ but this is not necessarily unreasonable.

Turning now to the dilute concentration regime, we would expect the measured diffusion coefficient to be inversely proportional to the hydrodynamic radius R_H of the polyion, according to (4). In Table IV we compare the values of R_H as derived from D_{eff}^0, the effective diffusion coefficient measured at the lowest concentration investigated, to R_F calculated according to (11). In all three cases $R_H < R_F$ although the ratio of the three values for R_H (1:1.2:2.2) with increasing M does not differ too much from that for R_F (1:1.2:1.9). Of course, it should be kept in mind that R_F is a limiting value for the mean dimension of the macromolecule in a good solvent and that furthermore (11) is given up to a numerical factor of order unity. It may be better to compare R_H to the root-mean-square radius of gyration $\langle S^2\rangle^{1/2}$ for an individual chain of finite length. For charged macromolecules the expressions for $\langle S^2\rangle^{1/2}$ derived by Odijk and Houwaart[24] may be used. It is also based on the wormlike chain approach. Values of $\langle S^2\rangle^{1/2}$ have been calculated (see Table IV) in this way, using, however, for the excluded volume parameter due to electrostatic repulsions between two Kuhn segments of the chain the expression proposed by Fixman and Skolnick[25]

$$\langle S^2\rangle = \alpha_s^{\,2}\langle S^2\rangle_0 \tag{24}$$

$$\langle S^2\rangle_0 = 2L_t l\left\{\frac{1}{6} - \frac{1}{2}\left(\frac{L_t}{l}\right) + \left(\frac{L_t}{l}\right) + \left(\frac{L_t}{l}\right)(e^{-l/L_t} - 1)\right\} \tag{25}$$

$$\alpha_s^{\,2} = 0.541 + 0.459(1 + 6.04Z_{\mathrm{el}})^{0.46} \tag{26}$$

$$Z_{\mathrm{el}} = \left(\frac{3^{3/2}}{16\pi^{1/2}}\right)\kappa^{-1}\left[\ln\left(\frac{4\pi}{Q\kappa}\right) + \gamma - \tfrac{1}{2}\right] l^{1/2} L_t^{\,-3/2} \tag{27}$$

Here, $\langle S^2\rangle_0$ is the mean square radius of gyration for an ideal wormlike chain according to Benoit and Doty[26] and α_s is the expansion factor for excluded volume effects. The latter is calculated according to the Yamakawa–Tanaka[27] expression (26) as function of the excluded volume parameter Z_{el}. This parameter is evaluated by (27) ($\gamma = 0.57721...$ is Euler's constant) based on only electrostatic repulsion. Note that in Odijk and Houwaart's paper the expression between square brackets in (27) is put equal to a constant. According to Fixman and Skolnick the

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argument of the logarithm in this expression is $4\pi Q/A^2\kappa$. We have applied here again the simple condensation approach so that for $\lambda > 1$, A^2 has to be replaced by its effective value Q^2, consistent with the assumptions used above.

It may be seen in Table IV that the values of $\langle S^2 \rangle^{1/2}$ still differ from R_H by a factor 1.5–2, which is not uncommon. Their ratio again does not deviate too much from that of R_H (1:1.3:1.9). Note that it would have been preferable to use instead of $D_{eff}{}^0$ the value obtained by a linear extrapolation to concentration zero of D_{eff} measured at several different concentrations in the dilute regime where D is a slightly increasing function of C and the extrapolated value of R_H would be closer to $\langle S^2 \rangle^{1/2}$ than shown in Table IV. Not enough measurements in the dilute regime were available to proceed likewise, however.

Finally, not much can be said concerning the transition region between the dilute and semidilute concentration regimes. We have insufficient results to allow any conclusion concerning the concentration and molar mass dependence of D_{eff}.

Conclusion

The results presented here are at least qualitatively consistent with the predictions of scaling theory for polyelectrolytes by showing the two distinct concentration regimes separated by a transition region around the value of C^*. In the semidilute regions the effective diffusion coefficient is definitely molar mass independent at constant salt concentration and seems to be determined by the correlation length ξ. It is difficult to assess the scaling law prediction more quantitatively particularly because the value of the intrinsic persistence length L_p is not known accurately. For $10 \times 10^{-8} \leq L_p \leq 50 \times 10^{-8}$ cm, a concentration power law is found with an exponent $0.80 \leq \nu \leq 0.76$, which is quite satisfactory.

In the dilute regime the effective diffusion coefficient of the polyelectrolytes reflects the translational behavior of individual polyelectrolyte chains. The hydrodynamic radius is somewhat smaller than the root-mean-square radius of gyration as calculated for a charged wormlike chain with excluded volume effects.

In a subsequent paper we shall study the effect of the salt concentration on the effective diffusion coefficient and compare these results with the theoretical predictions of scaling theory.

Registry No. NaPSS, 9080-79-9.

References and Notes

(1) de Gennes, P.-G. *Macromolecules* **1976**, *9*, 587.
(2) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953.
(3) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(4) Yu, T. L.; Reihanian, H.; Jamieson, A. M. *Macromolecules* **1980**, *13*, 1590.
(5) Adam, M.; Delsanti, J. *Macromolecules* **1977**, *10*, 1229.
(6) Nose, T.; Chu, B. *Macromolecules* **1979**, *12*, 590.
(7) Roots, J.; Nyström, B. *Polymer* **1979**, *20*, 148.
(8) Odijk, T. *Macromolecules* **1979**, *12*, 688.
(9) Odijk, T. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 477.
(10) Koene, R. S.; Smit, H. W. J.; Mandel, M. *Chem. Phys. Lett.* **1980**, *74*, 176.
(11) Berne, B.; Pecora, R. "Dynamic Light Scattering"; Wiley: New York, 1976.
(12) Batchelor, G. K. *J. Fluid Mech.* **1972**, *52*, 243. Pyun, C. W.; Fixman, M. *J. Chem. Phys.* **1964**, *41*, 937.
(13) Oosawa, F. "Polyelectrolytes"; Marcel Dekker: New York, 1972.
(14) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924.
(15) Nieuwenhuizen, P. *Macromolecules* **1978**, *11*, 832.
(16) Lacharojana, S.; Caroline, D. *Macromolecules* **1977**, *10*, 365.
(17) Bezot, P.; Ostrowsky, N.; Hesse-Bezot, C. *Opt. Commun.* **1978**, *25*, 14.
(18) Koppel, D. *J. Chem. Phys.* **1972**, *57*, 4814.
(19) Ackerson, B. *J. Chem. Phys.* **1978**, *69*, 684.
(20) Phillies, G. D. J. *Macromolecules* **1976**, *9*, 447.
(21) Hess, W. "Light Scattering in Liquids and Macromolecular Solutions"; Plenum Press: New York, 1980.
(22) Brown, J.; Pusey, D. N.; Dietz, N. *J. Chem. Phys.* **1975**, *62*, 1136.
(23) Odijk, T., private communication.
(24) Odijk, T.; Houwaart, A. C. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 627.
(25) Skolnick, J.; Fixman, M. *Macromolecules* **1977**, *10*, 944.
(26) Benoit, H.; Doty, P. *J. Phys. Chem.* **1953**, *57*, 958.
(27) Yamakawa, H.; Tanaka, G. *J. Chem. Phys.* **1967**, *47*, 3991.

Scaling Relations for Aqueous Polyelectrolyte–Salt Solutions. 2. Quasi-Elastic Light Scattering as a Function of Polyelectrolyte Concentration and Salt Concentration

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ABSTRACT: From quasi-elastic light scattering experiments on aqueous solutions of sodium poly(styrenesulfonate) ($M_w = 6.5 \times 10^5$ g mol^{-1}) in NaCl of various concentrations, the dependence of the effective diffusion coefficient of the polyion D_{eff} has been obtained as a function of the macromolecular (C) and salt (c_s) concentrations. At constant c_s dilute and semidilute regimes can be observed with increasing C. In the latter, D_{eff} increases with a concentration power law C^ν, where the exponent ν is close to the theoretical value 0.75 obtained from scaling considerations and is practically independent of c_s. The value of D_{eff} at constant C in the semidilute regime decreases with increasing c_s in a way that is not completely accounted for by the scaling theory for polyelectrolyte–salt systems. In the dilute regime D_{eff} is only slightly dependent on C but increases with c_s at constant C. This seems to be in agreement with the theoretically predicted decrease of the average dimensions of isolated polyelectrolyte chains.

Introduction

In a previous paper,[1] to be called part 1, it was shown that from quasi-elastic light scattering by aqueous solutions of sodium poly(styrenesulfonate) (NaPSS) in 0.01 M NaCl an effective diffusion coefficient can be derived. This diffusion coefficient exhibits a different concentration dependence in two distinct macromolecular concentration (c) regions separated by a transition region situated around

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