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Molar Mass and Ionic Strength Dependence of the Apparent Diffusion Coefficient of a Flexible Polyelectrolyte at Dilute and Semidilute Concentrations: Linear Poly(ethylenimine)

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ABSTRACT: The ionic strength and the molar mass dependence of the apparent diffusion coefficient of the polyelectrolyte linear poly(ethylenimine) is studied over a wide concentration range in 10, 25, and 100 mM NaCl solutions. At a constant NaCl concentration dilute and semidilute concentration regimes are distinguished with a different dependence of the diffusion coefficient on the polyelectrolyte concentration, the NaCl concentration, and the average molar mass of the polyelectrolyte. At infinite dilution the dependence of the diffusion coefficient on molar mass and on the added NaCl concentration are in good agreement with the theoretical predictions concerning the rms radius of gyration. At dilute concentrations the diffusion second virial coefficient is found to be inversely proportional to the NaCl concentration, which is in agreement with the theory taking into account the coupling of the motions of the small ions and the polyions. In the semidilute concentration regime the apparent diffusion coefficient is shown to follow a power law of the polyelectrolyte concentration and to be independent of the two molar masses investigated. The ionic strength dependence of the apparent diffusion coefficient was not in complete agreement with theory, but was shown to be consistent with previous measurements with NaPSS.

Introduction

In only a few dynamic light scattering studies has the behavior of the diffusion coefficient of synthetic flexible polyelectrolytes over a wide concentration range been systematically investigated. For flexible uncharged polymers the concentration dependence of the diffusion coefficient has been studied far more extensively by dynamic light scattering, revealing various concentration regimes with a different dependence on the concentration and molar mass.[1] Two concentration regimes are distinguished at low polymer volume fractions. In the dilute concentration regime, at the lowest polymer concentrations, the individual polymer coils remain separated in the solution and the diffusion coefficient is only weakly dependent on the polymer concentration. In the semidilute regime, at higher concentrations, the polymer coils interpenetrate and the diffusion coefficient shows a more pronounced dependence on the polymer concentration. In this regime the diffusion coefficient is found to be dependent on the polymer concentration to a certain power with a value between 0.5 and 0.75.

In polyelectrolyte solutions containined an abundant amount of added salt these two regimes can also be distinguished.[2,3] The polyion diffusion coefficient of Na-poly(styrene sulfonate) (NaPSS) solutions at NaCl concentrations in the range 100-10 mM shows a concentration dependence similar to that observed with uncharged macromolecules.[4,5] The interpretation of dynamic light scattering data and of the diffusion behavior of polyelectrolytes is however more complicated than that of neutral polymers, because of the influence of charge interactions which depend on the ionic strength of the solution.[2,3,5-7] This ionic strength dependence strongly influences the value of the diffusion coefficient at infinite dilution D_0 as well as the critical concentration c^*, around which the polyelectrolyte chains start to interpenetrate (the overall concentration c^*, which is directly related to the average dimensions at infinite dilution).

The polyelectrolyte used was linear poly(ethylenimine) (LPEI).

$$(\text{-CH}_2\text{-CH}_2\text{-NH-})_N$$

In the linear form branching of the chain is completely absent and the flexible backbone of the chain does not carry any substituents. When dissolved in aqueous solutions, LPEI can be charged (e.g. upon addition of HCl), by protonation of the secondary amino groups, the only type of amino groups present in this polyelectrolyte. The charges on the LPEI chain are positioned directly on the backbone of the chain, and not on bulky side groups as, e.g., with NaPSS, which can be of some significance for the ionic strength dependence of the polyelectrolyte conformation, as shown recently from the analysis of the titration curve for this polyelectrolyte.[8]

We here present experimental dynamic light scattering results obtained with two batches of LPEI with different molar masses, measured over a wide concentration range in solutions of 10, 25, and 100 mM NaCl. The object of this paper is to make a critical comparison between experimental results and theoretical predictions concerning the ionic strength, the molar mass, and the concentration dependence of the diffusion coefficient at infinite dilution, in the dilute and in the semidilute concentration regime. At infinite dilution and in the dilute concentration range a good agreement between the experimental results and theory is found. The behavior of the diffusion coefficient in the semidilute regime could not completely be explained but is consistent with the behavior of the diffusion coefficient in NaPSS solutions.[5]

Theory

A dynamic light scattering experiment probes the characteristic correlation time of the fluctuations of local optical inhomogeneities. In polymer solutions these optical inhomogeneities are caused by fluctuations in the distribution of the polymer, of which the characteristic correlation time yields information about the diffusion behavior of the solute macromolecules. The time dependent structure factor of scattered light from a polymer

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solution is defined by

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

where $\delta c(q,t)$ is the spatial Fourier transform of the local concentration fluctuations at time t, $\delta c^*(q,0)$ is its complex conjugate at $t = 0$, and $\langle ... \rangle$ stands for equilibrium statistical averaging; q is the magnitude of the scattering vector given by

$$q = \frac{4\pi n_s}{\lambda_0} \sin\left(\frac{\theta}{2}\right) \tag{2}$$

with λ_0 the wavelength of the incident light in vacuo, n_s the refractive index of the solvent, and θ the scattering angle. For a solution of noninteracting, identical, isotropic polymer coils, which are small compared to the wavelength of the light used, eq 1 can be written as

$$S(q,t) = S(q,0) \exp(-Dq^2 t) \tag{3}$$

with D the translational diffusion coefficient of the polymer coils. The value of the diffusion coefficient extrapolated to zero polymer concentration depends on the inverse of the average dimensions of an individual polymer coil. The diffusion coefficient of these polymer coils can be expressed as the diffusion coefficient of a spherical particle by introducing a hydrodynamic polymer coil radius R_h, which will be smaller than its root mean square (rms) radius of gyration R_g and given by the Stokes–Einstein equation.

$$R_h = kT/6\pi\eta D_0 \tag{4}$$

Here D_0 is the diffusion coefficient extrapolated to infinite dilution and η is the solvent viscosity.

Our first aim is to calculate the molar mass and the ionic strength dependence of the rms radius of gyration of the linear flexible polyelectrolyte from its diffusion coefficient extrapolated to infinite dilution, assuming a constant R_h/R_g ratio. A theoretical expression of R_g for linear flexible polyelectrolytes at intermediary salt concentrations, as a function of the ionic strength and the molar mass, has been given by Odijk.[2,6] The macromolecule is treated as a wormlike chain having discrete charges interacting according to the screened electrostatic Debye–Hückel potential. The influence of these electrostatic interactions on the average dimensions of the polyelectrolyte coil is attributed to two contributions: (a) a contribution due to charges separated less than the Debye–Hückel screening length κ^{-1} measured along the contour of the polyelectrolyte chain which influences the persistence length of the wormlike chain and (b) another contribution due to the charges separated by a distance along the chain larger than κ^{-1} which can increase the excluded polymer volume. The Debye–Hückel screening length κ^{-1} is defined as

$$\kappa^{-1} = (8\pi Q\mu)^{-1/2} \tag{5}$$

with μ the ionic strength of the solution due to the small ions only (in number of particles per volume). The Bjerrum length Q is the distance at which the electrostatic energy between two elementary charges equals kT,

$$Q = q^2/4\pi\epsilon\epsilon_0 k_b T \tag{6}$$

with q the elementary charge, ϵ the relative permittivity of the solvent, and ϵ_0 the absolute permittivity of free space. In aqueous solutions at a temperature $T = 298$ K the value of the Bjerrum length Q is 0.71 nm.

Contribution a is, in a first approximation, taken into account by letting the intrinsic persistence length L_p of the uncharged chain increase with a term L_e determined by electrostatic interactions.

$$L_t = L_p + L_e \tag{7}$$

This approximation is expected to hold if $L_t \gg \kappa^{-1}$. If the average distance between two consecutive charges on the polyelectrolyte chain is smaller than the Bjerrum length, counterion condensation according to Manning[9] can take place. For sufficiently long chains the electrostatic part of the persistence length is then given by

$$L_e = 1/4Q\kappa^2 \tag{8}$$

Contribution b is taken into account by the introduction of an electrostatic excluded volume parameter z_{el} as

$$z_{el} = \kappa^{-1} l^{1/2} L_t^{-3/2} \tag{9}$$

with l the contour length of the polyelectrolyte. This electrostatic excluded volume parameter is derived by assuming that all the long range interactions within the polyelectrolyte coil are of the electrostatic type and that the polyelectrolyte is locally rodlike on the length scale of $2L_t$ with an interaction radius equal to κ^{-1}.

The ionic strength dependence and the molar mass dependence of R_g of a polyelectrolyte coil is derived by using the theoretical Flory expression for the expansion factor in a good solvent for very large values of the excluded volume parameters.[1,10] With the assumption that the persistence length is given by L_t and the excluded volume parameter is determined by electrostatic interactions only, for $l \gg L_t$ the following expression for the rms radius of gyration is obtained to a constant of the order unity

$$R_g \simeq l^{1/2} L_t^{1/2} z_{el}^{1/5} \tag{10}$$

Substitution of eq 9 into eq 10 gives

$$R_g \simeq l^{3/5} L_t^{1/5} \kappa^{-1/5} \tag{11}$$

which is the expression of the radius of gyration of a long, highly charged flexible polyelectrolyte. Note that the theoretical molar mass dependence is the same as for neutral linear flexible polymers in good solvents.

In sufficiently *dilute* polyelectrolyte solutions the apparent diffusion coefficient measured by dynamic light scattering is determined by the average size of the coils and the interaction between the macromolecules. At low concentrations two particle interactions dominate and lead to a linear dependence of the diffusion coefficient on the polyelectrolyte concentration. This linear dependence of the apparent diffusion coefficient can be expressed in terms of the diffusion coefficient at infinite dilution D_0 and the diffusion virial coefficient k_d as

$$D = D_0(1 + k_d c) \tag{12}$$

with c the monomeric concentration of the polyelectrolytes in moles/liter. The lower the ionic strength the lower D_0, due to the increased expansion of the polyelectrolyte coils.

At higher polyelectrolyte concentrations the average bulk polyelectrolyte monomolecular concentration can become equal to the average monomolecular concentration within one single polyelectrolyte coil, so that a further increase of c is accompanied by *interpenetration* of the macromolecules. This determines a different concentration regime, called the *semidilute* concentration regime. For concentrations above the *overlap* polyelectrolyte concentration c^* defined as[1]

$$c^* \simeq \left(\frac{l}{hN_A}\right) \frac{10^{-3}}{{}^4/_3 \pi R_g^3} \tag{13}$$

with h the length of a monomeric unit and N_A the Avogadro constant, the interpenetration of the individual polyelectrolyte chains results in a transient physical network. In this network the dominating fluctuations contributing to the scattering of light are local, determined by screened parts of the chains of an average size ξ (called the *mesh size* or the network *correlation length*) which is assumed to be independent of l for sufficiently long polyelectrolyte chains.[1-3] As a consequence the diffusion coefficient will be inversely proportional to ξ, rather than depending on the inverse of the average size of the chains. The contour length independent mesh size of the transient network strongly decreases with increasing polyelectrolyte concentration according to a scaling law.

$$\xi \simeq R_g(c^*/c)^\nu \tag{14}$$

This scaling equation assumes that the value of R_g changes only slightly upon increasing the concentration below c^*. To estimate the diffusion coefficient at concentrations sufficiently above c^*, eq 4 is replaced by the following expression

$$\xi \sim kT/\eta D \tag{15}$$

with an unknown numerical factor. Combining eqs 14 and 15, we obtain for the diffusion coefficient in the semidilute regime

$$(D/D_0) \sim (c/c^*)^\nu \tag{16}$$

with the power ν determined by the condition that ξ, and thus also D, should be molar mass or l independent. Analogously for the case of neutral polymers in a good solvent,[1] $\nu = {}^3/_4$. Equation 16 should take into account the ionic strength and molar mass dependence of the reduced diffusion coefficient D/D_0, which is a universal function of the reduced concentration (c/c^*), as already used by Koene *et al.*[4,5] in a rather similar fashion.

Experimental Section

Materials. Two batches of LPEI·HCl have been synthesized with molar masses $M_w = (42.0 \pm 2.0) \times 10^3$ g/mol (520 monomeric units) and $M_w = (88.2 \pm 4.5) \times 10^3$ g/mol (1109 monomeric units), with the errors reflecting only the spread in the static light scattering data. They have been prepared by the polymerization of 2-phenyl-2-oxazoline following the method of Tanaka *et al.*,[11] with methyl trifluoromethanesulfonate as initiator.

The molar masses were determined in aqueous 1.0 M NaCl solutions by static low angle laser light scattering (LALLS) with a Chromatix KMX-6 and a 4-mW He–Ne laser ($\lambda = 632.8$ nm) at a temperature of 25 °C. The small scattering angle, less than 6°, allows for the use of the molecular structure factors with a value unity. Prior to the measurements the solutions were filtered through a 0.22-μm GV Millipore filter. The specific refractive index increment at 632.8 nm at the same NaCl concentration, determined with a Chromatix KMX-16 differential refractometer was found to be 0.22 ± 0.01 mL/g independent of molar mass.

The M_w/M_n ratio of 1.3 was determined by GPC for the low molar mass sample in 0.4 M NaCl, using a Superose-12 column from Pharmacia and a MALLS detector DAWN-F from Wyatt Technology. The DAWN-F detector was calibrated using the Rayleigh ratio of toluene at an angle of 90°. The angular sensitivity was normalized with well characterized Dextran samples. The M_w/M_n ratio of the highest molar mass batch was assumed to be approximately the same as that of the lower molar mass batch.

The ^{1}H NMR spectra of the LPEI batches in chloroform showed two major peaks, due to the methylene proton and the nitrogen proton, respectively, as expected for a linear chain of this composition, and a small third peak corresponding to protons of benzoyl residues in the polymer (less than 2.5%). This was also found by Tanaka.[11] Mass spectrometry for both LPEI·HCl batches gave the following composition: 31.3% C, 7.5% H, 15.7% N, 38.5% C, and 7.91% O. After drying the sample for 24 h at 100 °C, practically all the water was removed, resulting in a composition close to the theoretical one: 32.9% C, 7.4% H, 17.3% N, 39.3% Cl, and 0% O.

The LPEI·HCl concentration was adjusted by weight, taking into account 10 mass % water in the freeze dried samples. The concentration of LPEI·HCL solutions was independently checked by potentiometric titration with NaOH at a solution temperature of at least 55 °C. This temperature is the lowest temperature at which the LPEI is soluble in water over the complete charging range. The solutions of the 80% charged LPEI were dialyzed against the salt solutions to ensure a constant chemical potential upon dilution. After the dialysis the LPEI concentration was determined by measuring the increased weight of the total volume of the LPEI solution, which could be done within an accuracy of 1%. The decrease of the concentration due to filtration was less than 3%, as was measured by the change in the refractive index of the solution before and after filtration, and was neglected throughout.

Dynamic Light Scattering. The dynamic light scattering experiments were performed with a commercial apparatus consisting of a model ALV/SP-86#042 goniometer and an ALV-3000 correlator (ALV, Langen, Germany). The laser used as the light source was an argon-ion laser (Spectra Physics, Model 2000) operating at a wavelength of 514.5 nm. The autocorrelation functions of the scattered light intensity were recorded in the real time multiple τ mode with a time interval ranging from 0.8 μs to 50 s. A cylindrical quartz cuvette of 1-cm diameter was used, which during a measurement was thermostated at a temperature of 25 °C.

The solvent used was deionized water purified by a Milli-Q purification system, to which *pro analysi*, Merck NaCl was added. Before LPEI was dissolved, the solvent was first filtered through a Millipore VM 0.05-μm pore size filter. All samples were freshly prepared from dialyzed stock solutions that were kept frozen at −20 °C. After the dialysis the LPEI solutions were cleared of dust particles by filtering two to three times through a Millipore GV 0.2-μm pore size filter, which was first cleaned by flushing with Millipore water and the solvent. The cuvettes were rinsed with a 0.1 M HCl and a 0.1 M NaOH solution. Before every sample preparation the purification procedure of both the cuvette and the filter was tested by measuring the autointensity correlation function of Millipore water, which was not allowed to show any decay time during the typical measuring time of an experiment (minutes).

The intensity autocorrelation functions of 80% charged LPEI solutions with salt concentrations in the range 10–100 mM NaCl, showed one, almost exponential, decay mode, except at the highest LPEI concentrations. For these solutions an additional slower decaying mode was detected. This slow mode disappears after 2 or 3 weeks. Such solutions had therefore to be prepared a few weeks before the measurements.

Analysis of the Dynamic Light Scattering Data. The intensity autocorrelation functions, all slightly deviating from single exponential behavior, were analyzed by fitting to a cumulant expansion.[12,13]

If the scattered field is assumed to have Gaussian statistics, the normalized intensity autocorrelation function $g^{(2)}(\tau)$ is directly related to the normalized electric field autocorrelation function $g^{(1)}(\tau)$ through the Siegert relation.

$$g^{(2)}(\tau) = 1 + B|g^{(1)}(\tau)| \tag{17}$$

Here B is an equipment dependent amplitude factor.[14] For a system with noninteracting monodisperse pointlike particles the electric field autocorrelation function has a simple exponential form,

$$|g^{(1)}(\tau)| = \exp(-\Gamma\tau) \tag{18}$$

with a decay rate Γ directly proportional to the translational diffusion coefficient D of the single particles.

$$\Gamma = Dq^2 \tag{19}$$

If the deviation from the simple monoexponential behavior is attributable to the polydispersity of the polymer sample only, then for a continuous distribution of the molar mass $g^{(1)}(\tau)$ is given by

$$g^{(1)}(\tau) = \int A(\Gamma)\exp(-\Gamma\tau)\,d\Gamma \tag{20}$$

with $A(\Gamma)$ a weight factor of the contribution with the decay rate Γ normalized to unity as

$$\int A(\Gamma)\,d\Gamma = 1 \tag{21}$$

This $A(\Gamma)$ is a function of the number of particles giving a decay rate Γ at scattering vector q in the electric field autocorrelation function. Equation 20 can be expanded around the mean decay rate $\langle\Gamma\rangle$, defined as

$$\langle\Gamma\rangle = \int \Gamma A(\Gamma)\,d\Gamma \tag{22}$$

which leads to the cumulant expansion for the intensity autocorrelation function

$$g^{(2)}(\tau) = 1 + B\exp\left(-2\langle\Gamma\rangle\tau + \frac{2\mu_2}{2!\langle\Gamma\rangle^2}(\langle\Gamma\rangle\tau)^2 - \frac{2\mu_3}{3!\langle\Gamma\rangle^3}(\langle\Gamma\rangle\tau)^3 + \ldots\right) \tag{23}$$

Here μ_n is the nth order moment of the distribution of decay rates.

$$\mu_n = \int A(\Gamma)(\Gamma - \langle\Gamma\rangle)^n\,d\Gamma \tag{24}$$

The cumulant expansion is also valid if the deviations from single exponential behavior are not only determined by polydispersity. In that case the more general cumulant expansion is given by

$$g^{(2)}(\tau) = 1 + B\exp\left(-2K_1\tau + \frac{2K_2}{2!}\tau^2 - \frac{2K_3}{3!}\tau^3 + \ldots\right) \tag{25}$$

but the various cumulants have not the simple meaning as given by $\langle\Gamma\rangle$ and μ_n. If, however, the first moment K_1 is found to be proportional to q^2, one can determine an apparent diffusion coefficient D_{app} defined as

$$D_{app} = K_1/q^2 \tag{26}$$

In the analysis of our results the first three cumulants were obtained from a third order polynomial least squares fit of the logarithm of the intensity autocorrelation function minus 1.

$$\log(g^{(2)}(\tau) - 1) = \log B - 2\left(K_1\tau - \frac{K_2}{2!}(\tau)^2 + \frac{K_3}{3!}(\tau)^3 + \ldots\right) \tag{27}$$

The base line is thus assumed to have the value 1. Relative values with respect to K_1 of the second and third cumulant are of the order $(K_2/2!)/K_1 = 0.12$ and $(K_3/3!)/K_1 = 0.03$.

Two criteria were used to conclude that a fit with N data points is satisfactory. The first criterium is the value of the quality factor Q of the fit, defined as

$$Q = \frac{\sum_{i=1}^{N-1}(n_i - \tilde{n}_i)(n_{i+1} - \tilde{n}_{i+1})}{\sum_{i=1}^{N-1}(n_i - \tilde{n}_i)^2} \tag{28}$$

where n_i is the value of the ith experimental point of the autocorrelation function and $\tilde{n}_i$ its value according to the fitted curve. Fits with $Q \geq 0.75$ were assumed acceptable. The second criterium is the absence of systematic deviations in the residue plots of the fitted curves. An example of an intensity correlation function satisfying the two criteria is shown in Figure 1a.

Application to our results of the programs *Contin* or *Discrete*,[15] which are commonly used for autocorrelation analysis, resulted in one mode with an average correlation time consistent with the fit parameters found with the cumulant analysis. A two exponential fit of the experimental autocorrelation functions produced two decay rates differing no more than a factor 3. The average value of the two decay rates, weighted with the respective amplitude values, was equal to the first cumulant from the cumulant fit within experimental error.

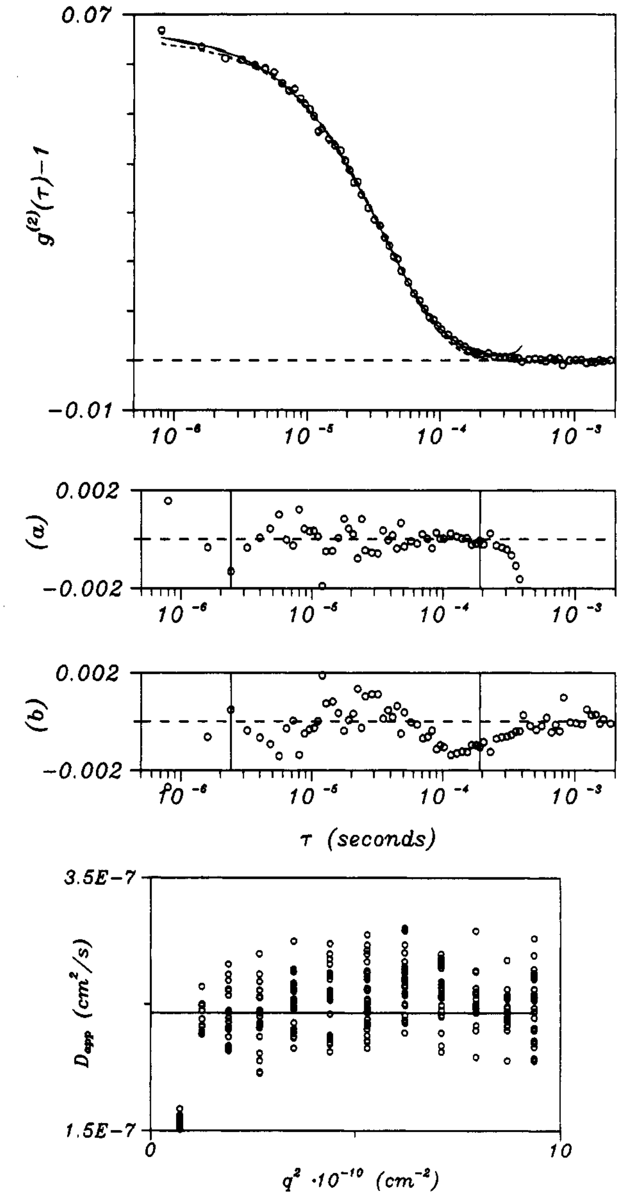

Figure 1. (a, top) Intensity autocorrelation function measured at 2.51×10^{-3} mol/L LPEI in 10 mM NaCl at a scattering angle of 90° (the average of four individually measured correlation functions). The drawn line is the fit result with three cumulants giving $D = 2.55 \times 10^{-7}$ cm²/s, $(K_2/2!)/K_1^2 = 0.09$, $(K_3/3!)/K_1^3 = -0.006$, and $Q = 0.89$, with (a) the residual plot. The dashed line is the result of the one exponential fit giving $D = 2.33 \times 10^{-7}$ cm²/s and $Q = 0.35$, with (b) the residual plot. The temperature was 25 °C. (b, bottom) D_{app} versus q^2 as measured for 2.51×10^{-3} mol/L LPEI in 10 mM NaCl (system with the largest spread in the data points). The result of the linear regression is $D_0 = 2.41$-(±8%) × 10^{-7} cm²/s and a slope of 2.1 (±0.6) × 10^{-10} cm⁴/s. The temperature was 25 °C. The large spread of the data is typical for the lowest LPEI concentrations measured in 10 mM NaCl and is due to the low excess scattering intensity. For this sample the excess scattering intensity was twice that of the scattering of the aqueous solvent. The values of D_{app} at the lowest q^2 values (scattering angle of 30°) are too small to be included in the fit. This was probably due to the presence of dust in the solution or spurious reflected light into the detector.

Every sample was measured several times over the angular range 40–140° (as with the cuvettes used measurements at the lower angles were not possible with aqueous solutions) resulting in about 150–250 intensity autocorrelation functions for each sample. The samples were purified to such an extent that at least 70% of the correlation functions satisfied the two criteria listed above.

For all the samples investigated D_{app} was determined at each angle using eq 26 and was found to be nearly independent of the measuring angle, as shown in Figure 1b, and the lines Γ versus q^2 passed through the origin within experimental error. All D_{app}

values used were nevertheless obtained by linear least squares extrapolation to a zero angle of D_{app} at all values of q^2.

Results

Both the ionic strength and the molar mass dependence of the apparent diffusion coefficient of the linear flexible polyelectrolyte LPEI was studied in the *dilute* and the *semidilute* concentration regime. The ionic strength dependence of the D_{app} was measured by dynamic light scattering of LPEI with a degree of polymerization of 520 in 10, 25, and 100 mM NaCl solutions. The molar mass dependence was investigated by comparing the results of the two batches of LPEI with different degrees of polymerization (520 and 1120) in 25 mM NaCl. An 80% degree of protonation of the polyelectrolyte chains was chosen, which did not vary more than 2% over the LPEI concentration range studied. At this degree of protonation the influence on the mean conformation of the polyelectrolytes in 100 mM NaCl is hardly influenced by direct specific interactions between neighbor and next-nearest neighbour charges.[8]

The different concentration regimes were recognized by the difference in the dependence of the total scattering intensity on the LPEI concentration at a constant NaCl concentration. At low LPEI concentrations the total scattering intensity was strongly increased by the increase of the LPEI concentration and this area was recognized as the dilute concentration regime. At higher LPEI concentrations (transition and semidilute regime) the scattering intensity depended only very weakly on the LPEI concentration. In the dilute regime D_{app} was found to depend on the ionic strength of the solution and to be linearly dependent on the polyelectrolyte concentration, as is shown in Figure 2a. At infinite dilution D_0, i.e. D_{app} extrapolated to zero LPEI concentration, decreases with decreasing ionic strength, as a result of the increased average dimensions of the individual polyelectrolyte coils due to the larger interactions of the charges on the polyelectrolyte chain. At lower NaCl concentrations the c dependence of D_{app} is much more pronounced than at higher NaCl concentrations. This difference in the concentration dependence of D_{app} in solutions of different salt concentrations results in the intersection of the three curves in Figure 2a.

In Figure 2b the concentration dependence of D_{app} is shown for the two different degrees of polymerization of LPEI. A definite molar mass dependence of D_0 is observed, with the lower values of D_0 for the higher molar mass. The slope of the concentration dependence of D_{app} does not seem to depend on the molar mass. The D_0 and k_d values of LPEI, obtained by linear regression of D_{app} versus c using the data represented in Figure 2a,b, are given in Table I.

At higher LPEI concentrations are c dependence of the apparent diffusion coefficient becomes far more pronounced, as is evident from Figure 3. The numerical data are given in the Appendix. For the highest LPEI concentrations studied the D_{app} satisfies a power law dependence on the polyelectrolyte concentration for all three ionic strengths and both molar masses studied. The concentration regime showing such a power dependence of D_{app} on c is identified as the semidilute concentration regime, as the diffusion coefficient is found to be independent of the degree of polymerization for the two LPEI molar masses investigated. The ionic strength dependence of the diffusion coefficient of LPEI in the semidilute concentration regime is more pronounced but with an opposite effect than at infinite dilution. The semidilute regime occurs already at lower polyelectrolyte concentrations in solutions of lower ionic strengths due to the ionic strength dependence of c^*. The theoretical values of c^* using eqs 11 and 13 are shown in Table I for the different experimental conditions.

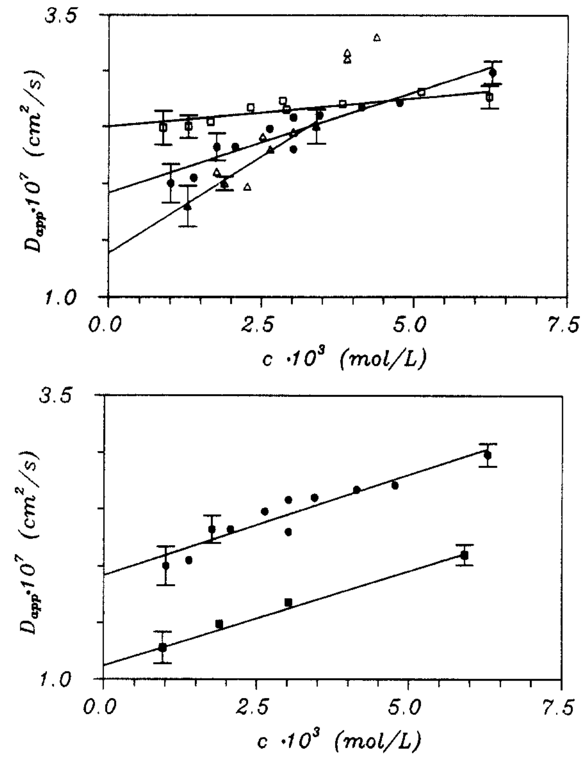

Figure 2. (a, top) Dependence of the apparent diffusion coefficient on the LPEI concentration in the dilute concentration regime at three different ionic strengths. The least squares fit results are given in Table I. $M_w = 41.5 \times 10^3$ g/mol: (△) in 10 mM NaCl, (●) in 25 mM NaCl, and (□) in 100 mM NaCl at a temperature of 25 °C. (b, bottom) Dependence of the apparent diffusion coefficient on the LPEI concentration in the dilute concentration regime for two different molar masses in 25 mM NaCl at a temperature of 25 °C: (●) $M_w = 41.5 \times 10^3$ g/mol, (■) $M_w = 88.2 \times 10^3$ g/mol. The least squares fit results are given in Table I.

Table I. Least Squares Linearly Extrapolated Value to $c = 0$ of Measured D_{app} at Dilute Concentrations (D_0) and Corresponding Slope k_d for Different LPEI Solutions at a Temperature of 25 °C[a]

	$10^7 D_0$, cm^2/s	$10^{-4} k_d$, L/mol	$10^3 c^*$, mol/L
$M_w = 41.5 \times 10^3$ g/mol, 100 mM NaCl	2.48 ± 0.06	0.23 ± 0.04	23.2
$M_w = 41.5 \times 10^3$ g/mol, 25 mM NaCl	1.92 ± 0.10	0.92 ± 0.10	11.1
$M_w = 41.5 \times 10^3$ g/mol, 10 mM NaCl	1.39 ± 0.12	2.5 ± 0.5	5.8
$M_w = 88.2 \times 10^3$ g/mol, 25 mM NaCl	1.12 ± 0.05	1.5 ± 0.1	6.0

[a] Also given are the values of c^* calculated according to eqs 11 and 13 with $L_p = 1$ nm.

The power law dependencies of D_{app} on c are revealed by the straight lines in the log–log plots of Figure 3 for $c > c^*$. These straight lines are obtained by the linear regression of the logarithm of the apparent diffusion coefficient against the logarithm of the LPEI concentration according to

$$\log(D_{app}) = \nu \log(c_p) + \delta \qquad (29)$$

The parameters of the linear regressions are shown in Table II. As can be seen, the values of the exponents are significantly larger than the theoretically predicted value of 3/4 and are only slightly dependent on the ionic strength of the solution, as they decrease somewhat with decreasing concentrations of NaCl. A similar observation was made by Koene *et al.*[5] in their study of the ionic strength

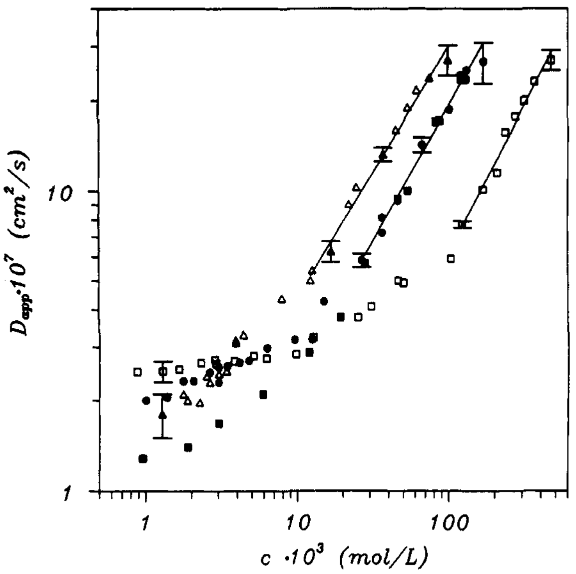

Figure 3. Dependence of the apparent diffusion coefficient on the LPEI concentration at three different ionic strengths and for two different molar masses at a temperture of 25 °C. The least squares fit results are given in Table III. $M_w = 41.5 \times 10^3$ g/mol: (△) in 10 mM NaCl, (●) in 25 mM NaCl, and (□) in 100 mM NaCl. $M_w = 88.2 \times 10^3$ g/mol: (■) in 25 mM NaCl.

Table II. Linear Least Squares Fit Parameters for the Logarithm of the Apparent Diffusion Coefficient of LPEI versus the Logarithm of the Concentration in the Semidilute Regime at a Temperature of 25 °C

$M_w = 41.5 \times 10^3$ g/mol, 100 mM NaCl	$\log(D_{app}) = (1.00 \pm 0.06)\log(c) - (8.22 \pm 0.03)$
$M_w = 41.5 \times 10^3$ g/mol, 25 mM NaCl	$\log(D_{app}) = (0.86 \pm 0.03)\log(c) - (7.46 \pm 0.03)$
$M_w = 41.5 \times 10^3$ g/mol, 10 mM NaCl	$\log(D_{app}) = (0.83 \pm 0.03)\log(c) - (7.19 \pm 0.03)$
$M_w = 88.2 \times 10^3$ g/mol, 25 mM NaCl	$\log(D_{app}) = (0.94 \pm 0.03)\log(c) - (7.60 \pm 0.03)$

dependence of the dynamic light scattering by NaPSS (M_w = 650 000 g/mol) solutions with NaCl concentrations in the range 10–100 mM.

In Figure 4 the diffusion coefficients rescaled according to eq 16 are represented as a function of c/c^* for the same data of LPEI as in Figure 3 and in the Appendix. The experimental D_0 values of Table I have been used, and the concentration is rescaled on the basis of the calculated value of c^* using eqs 11 and 13. A small molar mass dependence seems to be induced by the rescaling of the data, but it remains within the experimental error. The rescaling does not result in a proper ionic strength dependence correction, however, as for example, the difference between the rescaled data in 100 and in 10 mM NaCl differ by about a factor 2 in the ratio D_{app}/D_0.

Discussion

Infinite Dilution. Our first aim is to compare the molar mass and the ionic strength dependence of the experimental D_0 values with the theoretical predictions given in eq 11. To estimate the molar mass dependence of D_0, the ratio R_h/R_g is assumed to be constant in infinite dilute solutions for the two different molar masses of the LPEI investigated. With this assumption we expect D_0 to be proportional to $M^{-0.6}$ under good solvent conditions, with M the molar mass of the LPEI. This is strictly true for monodisperse samples, as otherwise the z-averaged diffusion coefficient and the weight-average molar mass of the polyelectrolyte are experimentally obtained. We have estimated, however, by assuming a Schultz distribution[16] to represent the molar mass distribution of the polymer batches with an M_w/M_n ratio of 1.3, that the error made by ignoring the polydispersity is smaller than 3%. For the two molar masses of LPEI investigated the exponent of the molar mass power law for the experimentally derived D_0 values is -0.7 ± 0.1, in good agreement with the theoretically predicted molar mass dependence. This value is, of course, not entirely trustworthy because only two samples of LPEI with different molar masses have been used.

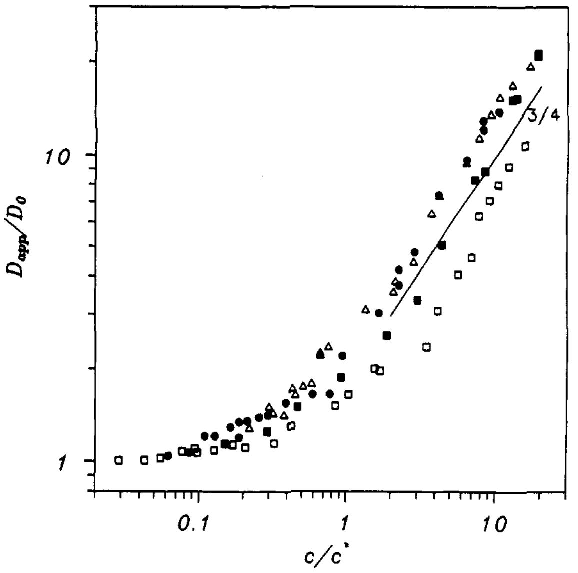

Figure 4. Dependence of the ratio of the apparent diffusion coefficient and the experimentally determined diffusion coefficient at zero LPEI concentration at a temperature of 25 °C on the ratio of the concentration of LPEI and the calculated value of C^* using eqs 11 and 13, at three different ionic strengths and for two different molar masses. $M_w = 41.5 \times 10^3$ g/mol: (△) in 10 mM NaCl, (●) in 25 mM NaCl, and (□) in 100 mM NaCl. $M_w = 88.2 \times 10^3$ g/mol: (■) in 25 mM NaCl.

Table III. Ratio of the Calculated Value of the Diffusion Coefficient According to Eqs 4, 11, and 30, and Various Values of L_p, to the Extrapolated Value D_0 for Different LPEI Systems at a Temperature of 25 °C

	D_{cal}/D_0 L_p = 0.5 nm	D_{cal}/D_0 L_p = 1.0 nm	D_{cal}/D_0 L_p = 2 nm
$M_w = 41.5 \times 10^3$ g/mol, 100 mM NaCl	1.00	0.91	0.82
$M_w = 41.5 \times 10^3$ g/mol, 25 mM NaCl	0.97	0.90	0.86
$M_w = 41.5 \times 10^3$ g/mol, 10 mM NaCl	1.01	0.99	0.94
$M_w = 88.2 \times 10^3$ g/mol, 25 mM NaCl	1.05	0.99	0.94

Unfortunately, the experimental ratio R_h/R_g could not be directly measured for LPEI with static light scattering, because of the too small R_g values. However due to the uncertainty on the numerical prefactor in the theoretical eq 11, the knowledge of the exact value for the ratio R_h/R_g is not really necessary for the comparison of the experimental and theoretical molar mass and ionic strength dependencies of D_0 as long as it remains *constant* as a function of μ and M_w. For reasons of simplicity we have assumed that

$$R_h/R_g = 0.537 \tag{30}$$

which is the value for this ratio derived by Akcasu and Han[17] for polymers in good solvents, also applies for infinite diluted LPEI solutions in the NaCl range 10–100 mM. The value of eq 30 seems to be satisfactory for LPEI, as shown in Table III. The same was observed for NaPSS by Wang and Bloomfield.[18]

In Table III the ratios of the calculated values of the diffusion coefficient D_{cal} using equations 4, 11, and 15, and the experimental D_0 values from Table I are compared. The average distance between neighboring charges on the 80% charged LPEI chain has been assumed to be smaller than the Bjerrum length and has been taken to be equal to 0.35 nm. For the bare persistence length L_p possible values equal to 0.5, 1, and 2 nm have been chosen. Despite the uncertainty on the value of the ratio R_h/R_g as given by eq 30 and on the value of the numerical prefactor in eq 11, the results of Table III show absolute values of the D_{cal}/D_0 ratios close to 1 for the two molar masses at various ionic strengths. In the L_p range 0.5–2 nm the exact L_p value seems of little importance on the calculation of the molar mass and ionic strength dependence of D_{cal}, as shown in Table III. The relative change in the ionic strength dependence of D_{cal} with L_p never exceeds 12%. The best agreement for the molar mass and ionic strength dependence of the D_{cal}/D_0 ratios in Table III is obtained for $L_p = 0.5$ nm. Though this is rather small, such a value of L_p is not unrealistic when compared to the intrinsic persistence length of poly(ethylene oxide) (PEO),[19] which has a chemical structure similar to that of LPEI.

At infinite dilution the contour length and ionic strength dependence of the diffusion coefficient of LPEI seems to be well described by eq 11. It is interesting to know whether the presented theory also describes the experimental data measured on other polyelectrolytes. For the ionic strength dependence of L_t as given in eq 8 good agreement between theory and experiment has been found by Maret and Weill.[20] They measured the persistence length of erythrocyte DNA with a molecular mass of $M_w = 4.2 \times 10^6$ g/mol, a contour length of $l \approx 2.16 \times 10^3$ nm, and an intrinsic persistence length of $L_p = 50$ nm in the concentration range 0.1–2000 mM added NaCl. The results obtained by Weill[21] applying the Cotton–Mouton effect with three different molecular masses of NaPSS ($L_p = 1.2$ nm) in the ionic concentration range 0.1–2000 mM NaCl did not agree with eq 8, the more complete expression[22] for the electrostatic contribution to the total persistence length, which is a function of the contour length for relatively short polyelectrolyte chains, being needed. The ionic strength dependence found in these measurements was, however, much smaller than that theoretically predicted. Most of these experiments were performed at NaPSS concentrations in the semidilute concentration regime, and the contribution of the counterions of NaPSS to the ionic strength of the solution was often much larger than that of the added NaCl.

Raziel and Eisenberg[23] have measured the ionic strength dependence of the radius of gyration of KPSS with a molecular mass of $M_w = 350\,000$ g/mol in the added salt range 0.005–1 M KCl with static light scattering, long before the derivation of eq 11. The ratio of the calculated R_g using eq 11 to their experimental R_g is 1.38 ± 0.05 for all six concentrations of KCl, over a total variation of R_g of about a factor 3 and despite the possible polydispersity of the samples used. (A ratio larger than the one found is not surprising, because the theoretical expression of R_g is valid up to a numerical factor of the order unity.) The same authors also investigated the molar mass dependence of R_g for KPSS in 0.5 M KCl ($2.5 \times 10^4 \leq M_w \leq 1.2 \times 10^6$ g/mol). Their results may be represented as a power dependence on M_w with an exponent 0.64 ± 0.5, in good agreement with the theoretical value 0.6. More recent measurements with NaPSS[24,25] and PAA[26] solutions reveal a linear dependence of R_g^2 on $c_s^{-1/2}$, with c_s the concentration of monovalent salt. This linear dependence agrees, within an error of 3%, with the theoretical ionic strength dependence of R_g^2 according to eq 11 in the added monovalent salt range 1.0–0.001 M if a value $L_p = 1$ nm is assumed.

Little is known about the ratio R_h/R_g for polyelectrolytes. Some measurements seem to confirm that this ratio is rather constant for flexible polyelectrolytes at infinite dilution in the c_s range of our interest. Wang and Hyuk[27] claim to have measured for NaPPS a ratio R_h/R_g which is more or less constant in the added salt range 10–150 mM. In the measurements of Mattoussi et al. with the flexible polyelectrolyte poly(xylene tetrahydrothiophenium chloride) in the NaCl range 10–100 mM,[28] the ratio R_h/R_g varies less than 5%. On the other hand Peitzsch *et al.*[25] reported a variation by about 25% of the ratio R_h/R_g at infinite dilution for NaPSS of a molar mass 780 000 g/mol in the NaCl concentration range 1000–10 mM.

The molar mass dependence of the diffusion coefficient in the added salt range 10–150 mM in NaPSS solutions at very low concentrations in the dilute regime has been measured by Wang and Hyuk using dynamic light scattering.[27] From these measurements a power dependence of the diffusion coefficient on the molar mass was concluded with an exponent of 0.6–0.66, close to the theoretical value (0.6), assuming a molar mass independence of the ratio R_h/R_g. The validity of the molar mass dependence of eq 11 has also been successfully tested by Wijmenga *et al.*[29] with NaPSS of $1.8 \leq M_w \leq 10.3 \times 10^5$ g/mol in 10 mM NaCl solutions, using electric birefringence decay measurements.

Dilute Regime. A theoretical expression to explain the concentration dependence of polyelectrolyte diffusion coefficients in solutions with an excess of added salt concentration has been proposed by Imai and Mandel.[30,31] Up to the linear terms in the polyelectrolyte concentration this expression is given by

$$\frac{D}{kT} = \frac{\left(\frac{\partial \Pi / kT}{\partial c}\right)}{(\omega_p + \omega_s)}(1 + {\gamma_p}^2 Z^2 (1 - (\omega_\pm/\omega_p + \omega_s))(c/2c_s) + ...) \tag{31}$$

with Π the osmotic pressure of the polyelectrolyte solution, γ_p the activity coefficient of the counterions in the salt free solution, Z the effective charge of the polyion, ω_p the friction of the polyelectrolyte, and $\omega_\pm$ the friction coefficients of the small ions which are assumed to have identical values. The definition of ω_s is more complicated, but it is proportional to $\omega_\pm$ and can in the first approximation be neglected with respect to ω_p. The osmotic compressibility factor may be expressed in terms of the osmotic second virial coefficient A_2.

$$(\partial \Pi / kT)/\partial c = 1 + 2A_2 c + ... \tag{32}$$

If the term $kT/(\omega_p)$ in eq 31 is taken equal to D_o, by neglecting hydrodynamic interactions and the concentration dependence of ω_p, eq 31 can be written as

$$D = D_0(1 + [4A_2 c_s + {\gamma_p}^2 Z^2 (1 - (\omega_\pm/\omega_p + \omega_s))](c/2c_s) + ...) \tag{33}$$

where two separate contributions determine the theoretical value of k_d defined in eq 12. One linear contribution stems from the second virial coefficient of osmotic pressure, and the other from the coupling between the motions of the small ions and the polyions. It is difficult to predict if one of these contributions will dominate the ionic strength dependence of k_d. If it is the osmotic pressure contribution, the ionic strength dependence of D would correspond to that of $2A_2$. By analogy with uncharged chains, A_2 is expected to be proportional to the volume of the individual coils. This would lead to a decrease of k_d proportional to R_g^3 or D_0^{-3}. This however does not provide a satisfactory explanation for the ionic strength dependence of the

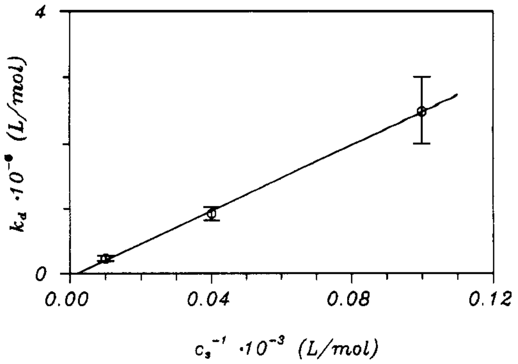

Figure 5. Dependence of the diffusion virial coefficient k_d on the inverse NaCl concentration c_s for $M_w = 41.5 \times 10^3$ g/mol at a temperature of 25 °C; the k_d values are given in Table I.

experimental k_d values. If, on the contrary, the ionic strength dependence of k_d is dominated by the coupling between the motions of the small ions and polyelectrolytes, eq 33 predicts k_d to be inversely proportional to the ionic strength, in agreement with the coupled mode theory of Schurr and Schmitz.[32] Experimentally, the dependence of k_d seems to be close to c_s^{-1}, as shown in Figure 5. However the error in the k_d value determined in 10 mM NaCl is too large to draw such a conclusion from the data given in Table I.

The same ionic strength dependence of k_d was also found by Slootmaekers *et al.*[33] from dynamic light scattering measurements on κ- and γ-carrageenan solutions in the added salt range 100–20 mM NaCl. This implies that the contribution of the osmotic second virial coefficient in eq 33 must either be negligible or also have a salt concentration dependence close to c_s^{-1}. The latter dependence has been deduced by Mattoussi *et al.*[28] from small angle light scattering measurements on the flexible polyelectrolyte poly(xylene tetrahydrothiophenium chloride). However Ghosh *et al.*[34] have measured an A_2 proportional to $c_s^{-0.5}$ by static light scattering measurements on the flexible polyelectrolyte hyaluronate, so it remains unclear which contributions in eq 33 determine the ionic strength dependence of k_d. Additionally, there could also be a contribution for the concentration dependence of ω_p.

Semidilute Regime. In the semidilute concentration regime of LPEI the ionic strength dependence is not completely controlled by the ionic strength dependencies of D_0 and c^*, as shown in Figure 4. In this figure the influence on the ionic strength of the solution of the noncondensed counterions provided by the polyelectrolytes has been ignored, as it cannot explain the deficiencies found between theory and experiment. This was noticed before by Koene *et al.*[5] for NaPSS. The correction on the ionic strength of LPEI does however have a significant influence on the values of the scaling exponents, which all increase and more closely approach unity.

Measurements of the concentration dependence of the diffusion coefficient for neutral polymers in the semidilute regime usually show a power law with the exponents varying between $^3/_4$ and $^1/_2$, depending on the solvent quality.[1] Larger exponential values than the theoretical $^3/_4$ have, however, been reported as well for neutral polymers.[35] Such stronger power dependencies have been interpreted in terms of three body interactions. It is possible that they are also responsible for the larger exponents in the polymer concentration power law found for LPEI.

To address the theoretical deficiencies in the salt concentration dependence of D_{app} in the semidilute concentration regime, even after the correction of the ionic strength, a comparison can be made between our measurements on LPEI, and measurements performed earlier in this laboratory by Koene *et al.*[4,5] They have determined the ionic strength dependence of the D_{app} of sodium poly(styrenesulfonate), NaPSS, with the degrees of polymerization of 1970, 3200, and 5900 in 10, 25, 50, and 100 mM NaCl solutions. In Figure 6 the ratio D_{app}/D_{cal} as function of the ratio c/c^* of the NaPSS measurements of Koene *et al.*[4,5] are shown together with the our results on LPEI. The values of D_{cal} and c^* of both LPEI and NaPSS have been calculated with the same theoretical expression as given above, using an identical L_p value of 1 nm to make the comparison easier. The rescaled data of LPEI and NaPSS show great resemblance. The rescaled data of NaPSS completely overlap the data of LPEI for the same NaCl concentration. In the semidilute concentration regime the D_{app} values of both polyelectrolytes show the same discrepancies with regard to theoretical predictions both for the polyelectrolyte and salt concentration dependence of D_{app}. Thus the power law exponent is larger than the predicted $^3/_4$ value. For both LPEI and NaPSS the exponents are found to be highest for the highest NaCl concentrations, and slightly decrease by lowering the salt concentration. It thus appears that there is a consistent behavior for the D_{app} of LPEI and NaPSS in the semidilute concentration regime, despite the chemical and physical differences between the two polyelectrolytes.

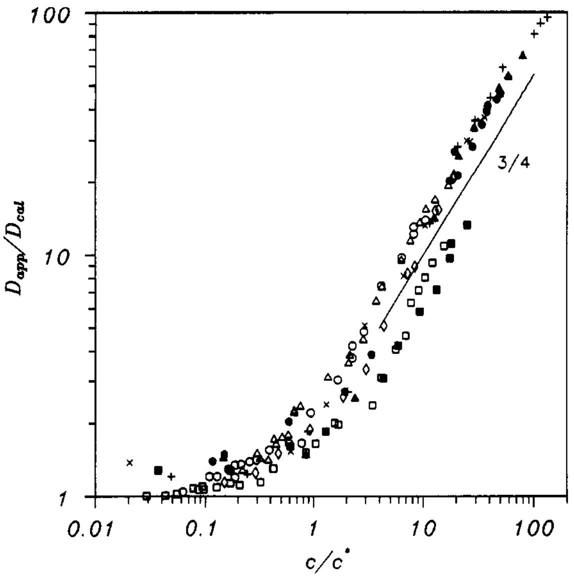

Figure 6. Dependence of D_{app}/D_{cal} on the ratio of the concentration of LPEI (open symbols) and NaPSS (closed symbols) and the calculated value of C^* for $L_p = 1$ nm at three different ionic strengths and for different molar masses of LPEI·HCl at a temperature of 25 °C. $M_w = 41.5 \times 10^3$ g/mol: (△) in 10 mM NaCl, (○) in 25 mM NaCl, and (□) in 100 mM NaCl. $M_w = 88.2 \times 10^3$ g/mol: (◇) in 25 mM NaCl. $M_w = 6.5 \times 10^5$ g/mol: (▲) in 10 mM NaCl, (●) in 25 mM NaCl, and (■) in 100 mM NaCl. $M_w = 1.2 \times 10^5$ g/mol: (+) in 10 mM NaCl. $M_w = 4.0 \times 10^5$ g/mol: (×) in 10 mM NaCl.

The corresponding discrepancies between theoretical predictions and measured salt concentration dependencies of D_{app} for both LPEI and NaPSS in the semidilute regime may originate from several weaknesses in the theoretical treatment. Thus, e.g., in eq 14 the influence of the salt concentration on the diffusion of the screened parts of the polyelectrolyte chain (the *blobs*) within a transient physical network has only be taken into account through the change of the correlation length ξ, neglecting the coupling between the charged blobs and the small ions. It cannot be excluded that the salt may also affect the friction coefficient of the blobs. Some support for this assumption may be found in the investigation by Koene *et al.*[36] who measured the osmotic pressure of NaPSS ($M_w = 6.5 \times 10^5$ g/mol) in 100,

Table IV. Apparent Diffusion Coefficient as a Function of LPEI Concentration, for Two Molar Masses and Three Different NaCl Concentrations at a Temperature of 25 °C

$M_w = 41.5 \times 10^3$ g/mol						$M_w = 88.2 \times 10^3$ g/mol, 25 mM NaCl	
100 mM NaCl		25 mM NaCl		10 mM NaCl			
10^3c, mol/L	10^7D, cm^2/s	10^3c, mol/L	10^7D, cm^2/s	10^3c, mol/L	10^7D, cm^2/s	10^3c, mol/L	10^7D, cm^2/s
465	27.0	170	26.7	99.4	27.1	122	24.0
365	23.0	132	25.0	75.7	23.7	122	23.4
313	20.0	132	23.4	62.4	21.6	88.5	17.2
274	17.7	103	18.7	54.6	19.0	82.7	17.0
234	15.7	67.3	14.3	45.0	16.0	54.1	10.0
208	11.5	46.4	9.26	37.2	13.3	46.4	9.38
169	10.1	36.5	8.10	24.8	10.3	28.2	5.70
124	7.70	36.5	7.20	22.0	9.00	19.4	3.76
104	5.89	26.8	5.83	16.7	6.24	11.9	2.88
50.7	4.90	15.1	4.24	12.6	5.40	5.91	2.10
46.6	4.98	12.5	3.18	12.2	4.99	3.02	1.68
31.2	4.09	9.54	3.17	7.95	4.35	1.89	1.40
25.4	3.76	6.29	2.98	4.39	3.30	0.96	1.28
12.8	3.23	4.76	2.71	3.90	3.10		
12.7	3.23	4.14	2.67	3.90	3.16		
9.74	2.84	3.44	2.60	3.39	2.50		
6.24	2.76	3.02	2.58	3.02	2.45		
5.12	2.81	3.02	2.30	2.64	2.30		
3.82	2.70	2.63	2.48	2.51	2.41		
2.90	2.65	2.06	2.32	2.26	1.97		
2.84	2.73	1.76	2.32	1.89	2.00		
2.31	2.67	1.38	2.05	1.76	2.10		
1.66	2.54	1.01	2.00	1.28	1.80		
1.29	2.50						
0.88	2.49						

50, 10, and 5 mM NaCl solutions for polyelectrolyte concentrations in the semidilute regime. Although, after the proper correction for the ionic strength, the osmotic measurements do not completely conform to the theoretical predictions, the discrepancies are smaller than those observed for the diffusion coefficient. This may be due to the fact that osmotic pressure is a static quantity and thus does not involve any correction for frictional effects.

Another cause for deviations from the theoretical predictions may originate in the variation of the solvent quality which could decrease at the higher NaCl concentrations. In the theory a good solvent is assumed, but a decrease in the solvent quality may affect the correlation length and thus also the value of D_{app}.[36] The reduction of the solvent quality could also induce a variation in the partial draining of the polyelectrolyte, which will reflect on the ionic strength dependence of D_{app}.

Ohta and Oono[37] have derived from renormalization group theory an expression to explain the concentration and the molar mass dependence of the osmotic compressibility of solutions of neutral polymers. This renormalization expression has been applied by Wang and Bloomfield[18] to the dynamic light scattering data of Koene *et al.*[4,5] using the static light scattering data of Takahashi *et al.*,[38] for NaPSS solutions in the salt concentration range 10–150 mM NaCl, to explain the polyelectrolyte concentration, molar mass, and salt concentration dependence of the measured diffusion coefficient in both the dilute and the semidilute regimes. Plotting rescaled quantities similar to the ones used in Figure 6, they found the same kind of deviations as observed in the work by Koene *et al.*[4,5] and here. A somewhat better agreement between theory and experiment is obtained if the polyelectrolyte concentration is rescaled according to the product k_dc rather than to $2A_2c \sim c/c^*$. A similar approach to our dynamic light scattering data of LPEI resulted in practically a theoretical molar mass and salt concentration dependence in the NaCl range 100–10 mM NaCl, given the experimental uncertainties on the measured quantities. The theoretical justification for this alternative rescaling is not obvious.

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Appendix

The dynamic light scattering data shown in Figure 3 are given in Table IV.

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