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ARTICLES

Molar Mass Dependence of the Apparent Diffusion Coefficient of Flexible Highly Charged Polyelectrolytes in the Dilute Concentration Regime

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In this study dynamic light scattering experiments have been performed on the flexible highly charged polyelectrolyte sodium poly(styrenesulfonate). The apparent diffusion coefficient was determined for five molar masses at a fixed ionic strength of 0.1 M at dilute polyelectrolyte concentrations. The apparent diffusion coefficients extrapolated to zero polyelectrolyte concentration were compared with theoretical D_0 values calculated with a theoretical procedure based on the translational friction coefficient of the wormlike chain model of Yamakawa and Fujii. With the excluded volume theories of Fixman and Skolnick, and Barrett, the electrostatic persistence length according to Le Bret, and the counterion condensation theory of Manning, a satisfactory agreement was found for all molar masses. From the polyelectrolyte concentration dependence of the apparent diffusion coefficient, the diffusion second virial coefficient could be obtained. The molar mass dependence of the diffusion second virial coefficient was found to be linearly proportional to the molar mass and could be interpreted with small ion−polyion coupled mode theories.

Introduction

The intensity autocorrelation functions measured with dynamic light scattering of flexible highly charged polyelectrolytes at high polyelectrolyte concentrations and low ionic strengths show two modes:[1] a fast and a slow mode. When the ionic strength increases and/or the polyelectrolyte concentration decreases, one mode is observed. Polyelectrolytes without added salt[2,3] show a similar behavior. However, in this case the transition from one mode to two modes occurs at very low polyelectrolyte concentrations, in the regime where the scattering intensity is very weak and reliable measurements can hardly be performed. To study the dilute concentration regime of flexible highly charged polyelectrolytes, one can measure at dilute polyelectrolyte concentrations and at relatively high ionic strengths.

The critical concentration c^* between the dilute and semidilute regime in polyelectrolyte solutions has been theoretically described by Odijk.[4] In the picture of Odijk only the fast mode is described. In the dilute concentration regime individual chains can be distinguished, whereas in the semidilute regime the chains interpenetrate. In the dilute regime the Brownian motion of the macromolecular chain can be experimentally studied by dynamic light scattering. From the autocorrelation function of the scattered light, one can obtain the dynamic structure factor.[5] This dynamic structure factor gives the apparent diffusion coefficient of the average individual chain.

A strong polyelectrolyte in solution dissociates fully into a polyion and numerous counterions. The addition of low molar salt results in the screening of the electric charges on the polyion. The conformation of the polyion depends on the chain length and on the screening of the charges. The persistence length of a polyelectrolyte characterizes the effective rigidity of the polyelectrolyte chain and involves short-range electrostatic interactions. Long-range electrostatic interactions are involved in the excluded volume. Due to counterion condensation, the number of effective charges on the polyelectrolyte chain is smaller than the number of fixed charges on the chain. This causes a change in the persistence length and excluded volume and also in the conformation of the polyelectrolyte.

In the dilute concentration regime the apparent diffusion coefficient of a polyelectrolyte depends on the chain length, ionic strength, linear charge density, polyelectrolyte concentration, and chemical structure. Several researchers[6−10] have reported apparent diffusion coefficients of flexible highly charged polyelectrolytes in the dilute concentration regime. In most studies only values for the apparent diffusion coefficient extrapolated to zero polyelectrolyte concentration D_0 have been reported. Data on the molar mass dependence of the apparent diffusion coefficient at finite dilute polyelectrolyte concentration are relatively scarce. In this work apparent diffusion coefficients of the strong polyelectrolyte sodium poly(styrenesulfonate) were obtained in aqueous solutions for five molar masses in the range from 46.4 to 350 kg/mol at a fixed ionic strength of 0.1 M at dilute polyelectrolyte concentrations. The moderate ionic strength of 0.1 M allows for the study of polyelectrolyte behavior. On the basis of dynamic light scattering measurements Wang and Yu[7] concluded that 3.1 M KCl is close to the θ-point at 25 °C. From the polyelectrolyte concentration dependence of the apparent diffusion coefficient, values for D_0 and k_d, the diffusion second virial coefficient, were obtained. The experimental D_0 values were compared with theoretical values, calculated with a theoretical procedure based on the translational friction coefficient of the wormlike chain model of Yamakawa and Fujii. The excluded volume theories of Fixman and Skolnick, and Barrett were applied including the electrostatic persistence length according to Le Bret and the counterion condensation theory of Manning. The experimental molar mass dependence of the diffusion second virial coefficient

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was qualitatively confronted with small ion−polyion coupled mode theories.

Experimental Section

Sodium poly(styrenesulfonate) (NaPSS) with different molar masses was purchased from Viscotek Benelux. The molar masses were 46.4, 77.4, 123, 168, and 350 kg/mol. The M_w/M_n ratios of the polyelectrolytes were smaller than 1.2. Nondialyzed samples contain a certain amount of sodium sulfate, and purification is necessary. In the purification procedure 1 g of NaPSS is dissolved in 0.2 M HCl (Baker Chemical Co.). This solution is dialyzed in a Visking seamless cellulose tubing against water, which was purified by a Milli-Q system. The dialysis bag was purified by heating in a solution of sodium bicarbonate (Merck), EDTA (Merck), and Millipore water, followed by extensive rinsing with Millipore water. The water surrounding the dialysis tube is refreshed several times, until the electric conductivity of this water equals the conductivity of pure water (the conductivity was always smaller than 1 μS/cm). Subsequently the dialyzed solution is converted to the sodium salt of PSS by potentiometric titration with 0.1 M NaOH (Titrisol), and the solution is stored freeze-dried. Ultrapure salt solutions with a concentration of 0.1 M were prepared by dissolving NaCl (Merck) in Millipore water. NaPSS solutions were prepared by dissolving the freeze-dried NaPSS in a salt solution. All samples were filtered through a Millipore GV 0.22 μm pore size filter, prior to the light scattering experiment. After the light scattering experiment the concentrations of the samples were determined spectrophotometrically at a wavelength of 261.5 nm, using an extinction coefficient of 1.92 ± 0.03 L g^{-1} cm^{-1}. The extinction coefficient was determined using the freeze-dried NaPSS. Infrared absorbance measurements were employed to determine the water content of the freeze-dried NaPSS, and the extinction coefficient was corrected accordingly.

Dynamic Light Scattering. The experimental setup for the dynamic light scattering measurements on the NaPSS solutions consists of an ALV goniometer (ALV, Langen, Germany), an ALV-5000 fast correlator, and a photomultiplier. The light source was an argon-ion laser (Spectra Physics Model 2020-03), operating at a wavelength of 514.5 nm in the light-stabilized mode. The filtered NaPSS solutions go directly into a cylindrical quartz cuvette with an outer diameter of 2 cm. Before and during each measurement the solution was thermostated at a temperature of 25 °C. Before each experiment the filtration setup and the quartz cuvette were cleaned with 0.1 M NaOH and extensively flushed with Millipore water. To check if the filtration setup and the cuvette were clean, Millipore water was filtered in a cuvette. After thermostating this water, the intensity autocorrelation function was measured. If this autocorrelation function does not show any decay time in the multiple tau mode, the filtration setup and the cuvette are considered clean and the NaPSS solution was filtered.

Analysis of the Dynamic Light Scattering Data. The ALV 5000 correlator calculates the normalized intensity autocorrelation function $g^{(2)}(\tau)$. For a system with noninteracting identical isotropic particles the normalized electric field autocorrelation function $g^{(1)}(\tau)$ is given by

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

Γ is a decay rate, related to the translational diffusion coefficient D,

$$D = \Gamma/q^2 \tag{2}$$

q is the magnitude of the scattering vector,

$$q = \frac{4\pi n_s}{\lambda_0}\sin\left(\frac{\theta}{2}\right) \tag{3}$$

n_s is the refractive index of the solvent, λ_0 is the wavelength of the incident light in vacuo, and θ is the scattering angle. However, polyelectrolyte and polymer samples are always polydisperse, and for a continuous distribution of the molar masses $g^{(1)}(\tau)$ is given by

$$|g^{(1)}(\tau)| = \int_0^\infty A(\Gamma)\exp(-\Gamma\tau)\,d\Gamma \tag{4}$$

with $A(\Gamma)$ a normalized distribution function of the decay rates. The Siegert relation relates the normalized intensity autocorrelation function $g^{(2)}(\tau)$ to the normalized electric field autocorrelation function $g^{(1)}(\tau)$, assuming the scattered field has Gaussian statistics.

$$g^{(2)}(\tau) = 1 + B|g^{(1)}(\tau)|^2 \tag{5}$$

B is an equipment dependent amplitude factor.

Equation 4 can be expanded around the average decay rate $\langle\Gamma\rangle$ defined as

$$\langle\Gamma\rangle = \int_0^\infty \Gamma A(\Gamma)\,d\Gamma \tag{6}$$

This yields, using the Siegert relation, the cumulant expansion for the normalized intensity autocorrelation function

$$g^{(2)}(\tau) = 1 + B\exp\left(-2\langle\Gamma\rangle\tau + \frac{2\mu_2}{2!\langle\Gamma\rangle^2}(\langle\Gamma\rangle\tau)^2 - \frac{2\mu_3}{3!\langle\Gamma\rangle^3} + ...\right) \tag{7}$$

μ_n is the nth-order moment of the distribution of decay rates,

$$\mu_n = \int_0^\infty A(\Gamma)(\Gamma - \langle\Gamma\rangle)^n\,d\Gamma \tag{8}$$

The cumulant expansion in eq 7 can also be used if the behavior of $g^{(1)}(\tau)$ is nonexponential.

For a relatively narrow distribution of decay rates the apparent diffusion coefficient is given by

$$D = \langle\Gamma\rangle/q^2 \tag{9}$$

The intensity autocorrelation functions measured in this investigation all deviate moderately from the exponential form. For all measurements we have used a third-order cumulant expansion. A fit is considered satisfactory if there are no systematic deviations in the plot of the residuals of the fitted curve. All samples were measured over the angular range from 30° to 150° with 10° increments. From the linear least-squares fit of $\langle\Gamma\rangle$ versus q^2 the apparent diffusion coefficients were obtained.

Results and Discussion

In this study we have determined the apparent diffusion coefficient of the flexible highly charged polyelectrolyte sodium poly(styrenesulfonate) at dilute polyelectrolyte concentrations. Five molar masses were used, and the ionic strength was fixed at 0.1 M. The separation between the dilute virial regime and the semidilute regime is indicated by the critical overlap concentration.[4] In this work the experiments were performed well below the molar mass and ionic strength dependent critical overlap concentration.

For each molar mass we have determined the apparent diffusion coefficient for several polyelectrolyte concentrations in the dilute regime. Figure 1 shows the apparent diffusion

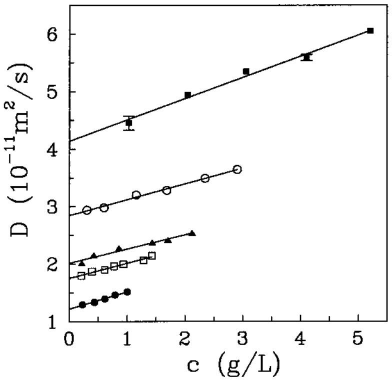

Figure 1. Apparent diffusion coefficient as a function of the NaPSS concentration for five molar masses: (■) M_w = 46.4 kg/mol, (○) M_w = 77.4 kg/mol, (▲) M_w = 123 kg/mol, (□) M_w = 168 kg/mol, and (●) M_w = 350 kg/mol. The ionic strength is 0.1 M. Drawn lines are linear least-squares best fits.

TABLE 1: Apparent Diffusion Coefficient at Infinite Dilution D_0 and the Diffusion Second Virial Coefficient k_d for Five Molar Masses at One Ionic Strength (0.1 M)

M_w (kg/mol)	D_0 (10^{-11} m²/s)	k_d (mL/g)
46.4	4.14 ± 0.08	89 ± 6
77.4	2.85 ± 0.02	96 ± 5
123	2.01 ± 0.03	121 ± 13
168	1.75 ± 0.02	146 ± 10
350	1.21 ± 0.01	244 ± 15

coefficient of five molar masses as a function of the polyelectrolyte concentration for one fixed ionic strength. In sufficiently dilute polyelectrolyte solutions it is observed that the apparent diffusion coefficient measured with dynamic light scattering is a linear function of the polyelectrolyte concentration:

$$D = D_0(1 + k_d c) \tag{10}$$

with D the apparent diffusion coefficient, D_0 the apparent diffusion coefficient at infinite dilution, k_d the diffusion second virial coefficient, and c the polyelectrolyte concentration. The polyelectrolyte concentration dependence of the apparent diffusion coefficient is linear for all conditions employed and shows that the virial expansion can be limited to the diffusion second virial coefficient in the concentration range studied. The drawn lines in Figure 1 are linear least-squares best fits, and values for D_0, the apparent diffusion coefficient extrapolated to zero polyelectrolyte concentration, could be obtained. The slope of each line divided by D_0 gives us according to eq 10 the diffusion second virial coefficient k_d. The obtained values for D_0 and k_d are collected in Table 1.

The molar mass dependence of the apparent diffusion coefficient extrapolated to zero polyelectrolyte concentration in 0.1 M NaCl is depicted in Figure 2. Note that both axes are logarithmic. Figure 2 shows that on increasing the molar mass D_0 becomes smaller. Although the experimental dependence of log D_0 on log M is not strictly linear, we find to a good first-order approximation in our molar mass range studied that D_0 is proportional to M^ν with $\nu = -0.61 \pm 0.04$. This result is in agreement with experimental data of Wang and Yu[7] for NaPSS in 0.15 M NaCl. The experimentally obtained power law is similar with the power law derived for polymers in a good solvent.[11]

In the section below we will give a procedure to calculate theoretical D_0 values. The polyelectrolyte is modeled as a wormlike chain of finite thickness. The theoretical procedure involves important conceptions such as the electrostatic persistence length and the electrostatic excluded volume. Since our system consists of highly charged polyelectrolytes, we also take counterion condensation into account. The theoretical diffusion coefficient at infinite dilution D_0 is related to the friction coefficient f by the Einstein relation

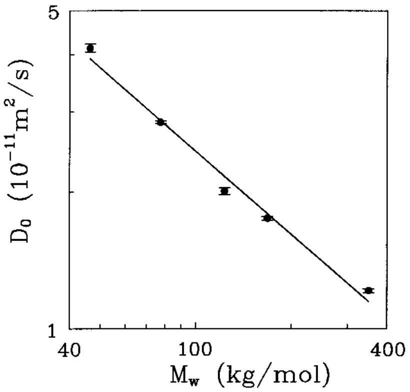

Figure 2. Apparent diffusion coefficient at infinite dilution D_0 as a function of the molar mass. The ionic strength is 0.1 M. The drawn line is the linear least-squares best fit.

$$D_0 = k_b T/f \tag{11}$$

where k_b is the Boltzmann constant and T the absolute temperature. The friction coefficient f of an excluded volume chain can be written as

$$f = \alpha_h f_0 \tag{12}$$

with f_0 the friction coefficient without excluded volume and α_h the hydrodynamic expansion factor. For f_0 the Yamakawa–Fujii theory[12] for the translational friction coefficient of a wormlike chain of finite thickness without excluded volume is used. This friction coefficient is a function of the number of Kuhn segments N_k, the chain contour length L, and the radius r of the polyelectrolyte, see the Appendix.

The hydrodynamic expansion factor α_h depends on the excluded volume parameter z,

$$z = \frac{3^{3/2}}{32\pi^{3/2}}\beta L^{1/2} L_t^{-7/2} \tag{13}$$

with L_t the total persistence length. The excluded volume β between Kuhn segments with length $2L_t$ is given in the Appendix. To calculate the hydrodynamic expansion factor, we can use the Barrett equation[13]

$$\alpha_h = (1 + 6.09z + 3.59z^2)^{0.1} \tag{14}$$

To calculate theoretical D_0 values, values for the total persistence length and a value for the radius r of the polyion are needed. We use the value of 9 Å for the radius of NaPSS. This value can be estimated from the bond lengths in NaPSS taking into account a possible layer of water molecules or counterions around the polyelectrolyte chain. For polyelectrolytes the total persistence length L_t is written as[14]

$$L_t = L_0 + L_e \tag{15}$$

The total persistence length represents the effective rigidity of the polyelectrolyte as the sum of two contributions: the intrinsic persistence length L_0 due to the rigidity of the uncharged chain and the electrostatic persistence length L_e arising from the repulsion between the ionic sites.

Le Bret[15] has calculated the electrostatic persistence length for a toroid by a numerical procedure on the basis of the

TABLE 2: Theoretical D_0 Values without and with Excluded Volume and the Total Persistence Length According to Le Bret for Five Molar Masses at c_s = 0.1 M

M_w (kg/mol)	L_t (Å)[a]	D_0 (10^{-11} m^2/s)[b]	D_0 (10^{-11} m^2/s)[c]
46.4	26.6	5.16	4.12
77.4	26.6	3.99	3.09
123	26.6	3.17	2.37
168	26.6	2.71	1.98
350	26.6	1.88	1.30

[a] Calculated with L_0=12 Å. [b] Calculated without excluded volume. [c] Calculated with excluded volume.

complete Poisson−Boltzmann equation. His results for the electrostatic persistence length are given in Tables I and II of ref 15 as a function of the polyion radius, the Debye−Hückel screening length, and the charge parameter. The data in his Tables I and II are calculated for a polyion radius of 10 Å. The electrostatic persistence length can be calculated for other values of the polyion radius. For Manning's counterion condensation[16] the charge parameter is 1, and we have calculated the electrostatic persistence lengths for a polyion radius of 9 Å at the ionic strength range in the region of our ionic strength. From interpolation of these data the electrostatic persistence length at our ionic strength of 0.1 M was obtained. We cannot apply the Odijk−Skolnick−Fixman[14,17] (OSF) electrostatic persistence length calculation since the OSF electrostatic persistence length has been derived for a line charge, while our theoretical procedure views the polyelectrolyte as a wormlike chain of finite thickness.

Now we are able to calculate theoretical D_0 values. For the intrinsic persistence length a value of 12 Å[18,19] is used. Theoretically calculated D_0 values using the electrostatic persistence length according to Le Bret, with and without the excluded volume correction, are summarized in Table 2. The monomer contour distance was 2.5 Å. The radius of the polyion is set to 9 Å, taking into account a possible layer of immobile water molecules or counterions around the polyelectrolyte chain. A change in the D_0 value of about 3% is found when this radius varied between 8 and 10 Å. The calculated D_0 values without excluded volume correction are much larger than the experimental D_0 values. Correction for the excluded volume effect leads to values that are close to the experimental values. The agreement is remarkable. Comparing the values for all molar masses, we see that the theoretical values are on average about 10% larger than the experimental values in the range of molar masses studied.

The polyelectrolyte is viewed as a chain consisting of rodlike segments with radius r and length $2L_t$. The excluded volume β is valid for rods. This means that the Kuhn segment must be rodlike. The validity of this condition becomes questionable at high ionic strengths. For example, at our ionic strength the total persistence length is about 27 Å and the Kuhn segment has a length of 54 Å and a diameter of 18 Å.

It could be conceived that the amount of condensed counterions depends on the length of the rodlike chain segment, since the application of the counterion condensation theory of Manning is strictly speaking only valid for infinitely long rods. In our case the chain segment length is about 54 Å, while the number of chain segments varies from about 11 for the lowest molar mass to about 80 for the highest molar mass. In this case the amount of condensed counterions could be smaller than Manning's theory predicts and the effective linear charge density will be larger than $1/Q$. We note that a larger value than $1/Q$ for the effective linear charge density yields a smaller value for the calculated D_0 value, and the deviations from the experimental values become even smaller.

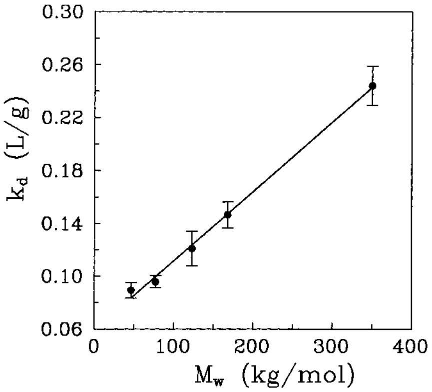

Figure 3. Diffusion second virial coefficient k_d as a function of the molar mass. The ionic strength is 0.1 M. The drawn line is the linear least-squares best fit.

We have given two possible explanations for the discrepancies we found between the theoretical and experimental D_0 values. The validity of the excluded volume and the counterion condensation criterion can become questionable at the ionic strength of 0.1 M. These two phenomena occur simultaneously due to a small segment length relative to the diameter of the polyelectrolyte. Nevertheless, we find a satisfactory agreement between the experimental and theoretical D_0 values. This same theoretical procedure could also be used to interpret measurements on NaPSS involving the ionic strength dependence of the apparent diffusion coefficient at infinite dilution.[20]

In our theoretical procedure to calculate D_0 we have used a value of 2.5 Å for the monomer contour length. With small angle neutron scattering on semidilute PSS solutions without added salt a value of about 1.7 Å for the *z*-axis projected distance between monomers has been determined.[21,22] We have also used this value for the monomer contour length in all our theoretical calculations. The theoretical D_0 values with the excluded volume correction then lead to values that are much larger than the experimental D_0 values. Recently, Spiteri et al.[23] have determined with small angle neutron scattering on semidilute PSS solutions with added salt a monomer contour length of 2.46 Å. It should be noted that the small angle neutron scattering results were obtained on much more concentrated solutions that possibly contained aggregates.[24]

Figure 3 shows that the experimental diffusion second virial coefficient is a linear function of M. To find an interpretation for this relationship, we address some small ion−polyion coupled mode theories. According to the coupled mode theory as derived by Lee and Schurr,[25,26] the apparent diffusion coefficient is approximated as

$$D \simeq D_0\left(1 + \left[1 - \frac{D_0}{D_s}\right]\frac{c_p Z^2}{2c_s}\right) \qquad (16)$$

with c_p the polyelectrolyte molarity and D_s the small ion diffusion coefficient. Since D_s is 2 or 3 orders of magnitude larger than D_0, the term $1 - D_0/D_s$ can be approximated as unity. Substituting c_p by c/M with c the polyelectrolyte concentration in g/L and M the molar mass in g/mol, the diffusion second virial coefficient k_d as defined by eq 10 can be approximated as $Z^2/(2Mc_s)$.

The molecular theory of Imai and Mandel[27,28] also predicts this. Since this is not obvious at first sight, we will elaborate this in some detail below. Imai and Mandel have derived a molecular theory for the effective diffusion coefficient of polyelectrolytes with excess added salt. The theory is valid only in dilute solutions. The approximate expression[28] obtained for the effective diffusion coefficient up to the linear terms in the polyelectrolyte concentration is

$$\frac{D}{k_bT} \simeq \frac{\frac{M}{N_a}\frac{\partial \Pi/k_bT}{\partial c}}{(\omega_p + \omega_s)}\left(1 + \frac{\gamma_p^{\,2}Z^2}{M}\left[1 - \frac{\omega_\pm}{\omega_p + \omega_s}\right]\frac{c}{2c_s} + ...\right) \quad (17)$$

with Π the osmotic pressure of the polyelectrolyte solution, M the molar mass of the polyelectrolyte, Z the number of elementary charges on the polyion, c_s the added salt concentration, γ_p the activity coefficient of the counterions in the salt-free solution, k_b the Boltzmann constant, T the absolute temperature, N_a Avogadro's number, and ω_p the friction coefficient of the polyelectrolyte. The friction coefficients of the small co- and counterions, $\omega_\pm$, are assumed to have identical values. The definition of ω_s is more complicated, but it is proportional to, and on the same order as, $\omega_\pm$.

Equation 17 contains the derivative of Π with respect to c. The classic virial expansion for the osmotic pressure is

$$\frac{M\Pi}{N_a k_b T} = c(1 + A_2Mc + ...) \quad (18)$$

with A_2 the osmotic second virial coefficient. For very dilute solutions the osmotic second virial coefficient contribution can be neglected (i.e. the osmotic pressure is well represented by the van 't Hoff expression). Substituting reasonable estimates for the parameters in the term A_2Mc, we can estimate this contribution. A typical value[10,29] for the osmotic second virial coefficient of NaPSS in 0.1 M NaCl is on the order of 5×10^{-4} mol ml g^{-2}. The estimated value for the term A_2Mc is about 0.05. Neglecting the term A_2Mc, $(M/N_a)\partial(\Pi/k_bT)/\partial c$ in eq 17 equals unity, so the theoretical diffusion second virial coefficient as defined by eq 10 is well approximated by

$$k_d \simeq \frac{\gamma_p^{\,2}Z^2}{2Mc_s}\left[1 - \frac{\omega_\pm}{\omega_p + \omega_s}\right] \quad (19)$$

It is likely that the polyion friction coefficient ω_p is much larger than ω_s or $\omega_\pm$, so the value between square brackets will only slightly deviate from 1. The activity coefficient γ_p of the counterions in a salt-free solution does not depend on the molar mass.[30] Equation 19 shows then that k_d is proportional to $Z^2/(2Mc_s)$, in agreement with the coupled mode theory of Lee and Schurr. When M/M_m, with M_m the monomer mass, is substituted for Z, it is readily seen that k_d has to be proportional to M. When we go back to the theoretical procedure to calculate D_0, we saw a good agreement between the theoretical and experimental D_0 values. In the calculation we assumed Manning's counterion condensation. This means that there is one effective charge per Bjerrum length. From our experimental D_0 values it can be concluded that the effective linear charge density is independent of the molar mass. So, when Z is replaced by the number of fixed charges on the chain or by the number of effective charges, k_d will be proportional to M. In the molar mass range studied a linear proportionality between k_d and M is observed, in agreement with the theoretical predictions.

Conclusions

In this investigation it is shown that the apparent diffusion coefficient of sodium poly(styrenesulfonate) in 0.1 M NaCl is a linear function of the polyelectrolyte concentration in the dilute concentration regime and depends strongly on the molar mass. The experimentally determined apparent diffusion coefficients extrapolated to zero polyelectrolyte concentration were compared with theoretical values calculated with a theoretical procedure based on the translational friction coefficient of the wormlike chain model of Yamakawa and Fujii. With the excluded volume theories of Fixman and Skolnick, and Barrett, the electrostatic persistence length according to Le Bret, and the counterion condensation theory of Manning, a satisfactory agreement was found for all molar masses. The diffusion second virial coefficient was found to be linearly proportional to the molar mass and could be interpreted with small ion−polyion coupled mode theories.

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Appendix

The Yamakawa−Fujii Theory for the Translational Friction Coefficient of a Wormlike Chain. Yamakawa and Fujii[12] have derived a procedure to calculate the translational friction coefficient of a wormlike chain of finite thickness without excluded volume by applying the Oseen−Burgers procedure of hydrodynamics to wormlike cylinder models. The wormlike chain is represented as a flexible cylinder with contour length L and radius r. Their expression for the translational friction coefficient f_0 for the wormlike chain with N_k Kuhn lengths reads for $N_k > 2.278$

$$\frac{3\pi\eta_0 L}{f_0} = A_1{N_k}^{1/2} + A_2 + A_3{N_k}^{-1/2} + A_4{N_k}^{-1} + A_5{N_k}^{-3/2} \quad (20)$$

and for $N_k \le 2.278$

$$\frac{3\pi\eta_0 L}{f_0} = C_1 \ln\left(\frac{N_k}{d}\right) + C_2 + C_3N_k + C_4{N_k}^2 + C_5{N_k}^3 + C_6\left(\frac{d}{N_k}\right)\ln\left(\frac{N_k}{d}\right) + C_7\left(\frac{d}{N_k}\right) + C_8\left(\frac{d}{N_k}\right)^2 + C_9\left(\frac{d}{N_k}\right)^3 + C_{10}\left(\frac{d}{N_k}\right)^4 \quad (21)$$

with η_0 the viscosity of the solvent. The coefficients A_1, ..., A_5 and C_1, ..., C_{10}, which are functions of the reduced diameter $d = r/L_t$, are given in ref 12. The number of Kuhn lengths $N_k = L/2L_t$, with L_t the total persistence length.

The Excluded Volume. The excluded volume β between Kuhn segments with length $2L_t$ is approximated as $\beta = \beta_0 + \beta_e$, where β_0 represents hard-core interactions and β_e electrostatic interactions. The hard-core part[31] is given by $\beta_0 = 4\pi {L_t}^2 r$, with r the radius of a rod segment. Fixman and Skolnick[32] have calculated for the binary cluster integral β_e

$$\beta_e \simeq 8{L_t}^2\kappa^{-1}R(\omega) \quad (22)$$

where $R(\omega)$ is given as

$$R(\omega) = \int_0^{\pi/2}\sin^2\theta \int_0^{\omega/\sin\theta} x^{-1}(1 - e^{-x})\, dx\, d\theta \quad (23)$$

with Manning's counterion condensation[16] $\omega = (2\pi/Q)\kappa^{-1}e^{-2\kappa r}$. In eq 22 κ^{-1} is the Debye−Hückel screening length. The Bjerrum length $Q = 7.135$ Å for water at 25 °C.

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