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 $D_{\text{eff}}{}^0$ 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 $10 \times 10^{-8} \le L_p \le 50 \times 10^{-8}$ cm, a concentration power law is found with an exponent $0.80 \le \nu \le 0.76$, 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.

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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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a critical concentration c^* inversely proportional to the cube of the Flory radius (R_F). This is in agreement with the prediction of scaling theory.[2] In the dilute concentration regime the diffusion coefficient D_{eff} was found to be only slightly increasing with c and decreasing with molar mass, in fair agreement with theory. In the semidilute region D_{eff} increases rather considerably with c and is independent of molar mass, a major requirement of scaling theory. A more quantitative check of the predictions of scaling theory in the semidilute region was rendered somewhat more difficult by the fact that the value of the intrinsic persistence length L_p of PSS has not yet been well established and that under experimental conditions no large excess of low molar mass salt was present. Nevertheless, the concentration power law of D_{eff} was in satisfactory though not complete agreement with the theoretical prediction for reasonable values of L_p ($10^{-7} \leq L_p \leq 5 \times 10^{-7}$ cm).

In the present paper we report an investigation of the influence of the low molar mass salt concentration c_s on D_{eff} of the PSS ion of a given molar mass in order to check the scaling relation derived by Odijk[3] for polyelectrolyte–salt solutions. According to this theory, ionic strength affects D_{eff} at $c \gg c^*$ through a factor $(L_t/\kappa)^{0.25}$ only. Here, L_t is the total persistence length of the charged polyelectrolyte chain. Therefore $D_{eff}(\kappa/L_t)^{0.25} \equiv B$ should be independent of ionic strength in the semidilute regime, a condition that can, in principle, be easily checked. In the dilute concentration regime D_{eff} should increase with ionic strength as the size of the individual particles decreases. As will be shown the latter is also found experimentally as well as the different concentration dependence of D_{eff} for $c \ll c^*$ and $c \gg c^*$. The value of B in the semidilute region was, however, found to be still dependent on c_s, in disagreement with theory. This discrepancy will be discussed in the last section.

Experimental Section

The materials are the same as in part 1. Quasi-elastic light scattering measurements were performed with a sample of NaPSS of molar mass 6.5×10^5 g mol^{-1} (Pressure Chemical Co.) as described in part 1. Four different NaCl concentrations were used ($0.01 \leq c_s \leq 0.1$ mol L^{-1}).

The data analysis was identical with that of part 1. The experimental correlation curves were definitely nonexponential. The cumulant analysis method revealed that the normalized second cumulant was not very sensitive to c_s and under all circumstances of the order 0.3, irrespective of c_s or c. It was observed that for the highest salt concentrations (0.05 and 0.1 M), solutions in the semidilute region, especially at the higher polyelectrolyte concentrations, had surprisingly large viscosities (notwithstanding the high ionic strength) and that the cleaning procedure was particularly difficult and slow. Measurements at these concentrations were more difficult to reproduce than at lower c_s.

Results

For each salt concentration c_s (in mol L^{-1}) several solutions of different polyelectrolyte concentration C (in g L^{-1}) were investigated. These concentrations were chosen in such a way that some are below and some above the critical concentrations C^*

$$C^* \simeq a^{-1} l^{-4/5} (L_t/\kappa)^{-3/5} \left(\frac{10^3 M_m}{N_A} \right) \qquad (1)$$

Table I
Effective Diffusion Coefficient of NaPSS ($M_w = 6.5 \times 10^5$ g mol^{-1}) in 0.1 M NaCl[a]

C, g L^{-1}	$10^8 D_{eff}$, cm^2/s	C, g L^{-1}	$10^8 D_{eff}$, cm^2/s
0.05	10.1 ± 0.1	12.6	46.0 ± 0.45
0.23	10.1 ± 0.1	17.9	56.6 ± 0.50
0.82	12.7 ± 0.13	23.7	76.5 ± 0.80
1.74	14.6 ± 0.15	24.3	88.0 ± 0.85
5.90	24.4 ± 0.25	33.9	105.0 ± 1.0
8.00	33.4 ± 0.3		

[a] $C^* = 5.64$ g L^{-1} for $L_p = 10^{-7}$ cm, 3.3 g L^{-1} for $L_p = 3 \times 10^{-7}$ cm, and 2.5 g L^{-1} for $L_p = 5 \times 10^{-7}$ cm.

Table II
Effective Diffusion Coefficient of NaPSS ($M_w = 6.5 \times 10^5$ g mol^{-1}) in 0.05 M NaCl[a]

C, g L^{-1}	$10^8 D_{eff}$, cm^2/s	C, g L^{-1}	$10^8 D_{eff}$, cm^2/s
0.28	9.2 ± 0.01	20.6	113 ± 1.0
1.92	12.8 ± 0.01	20.9	119 ± 1.1
8.89	56.2 ± 0.6	22.9	132 ± 1.3
13.3	87.7 ± 0.8	30.0	146 ± 1.5
17.7	86.3 ± 0.8		

[a] $C^* = 4.0$ g L^{-1} for $L_p = 10^{-7}$ cm, 2.5 g L^{-1} for $L_p = 3 \times 10^{-7}$ cm, and 1.9 g L^{-1} for $L_p = 5 \times 10^{-7}$ cm.

Table III
Effective Diffusion Coefficient of NaPSS ($M_w = 6.5 \times 10^5$ g mol^{-1}) in 0.025 M NaCl[a]

C, g/L	$10^8 D_{eff}$, cm^2/s	C, g/L	$10^3 D_{eff}$, cm^2/s
0.075	8.64 ± 0.09	12.3	168 ± 1.5
0.096	9.23 ± 0.09	18.0	176 ± 1.5
0.38	12.6 ± 0.10	21.8	217 ± 2.0
1.24	16.8 ± 0.15	24.2	246 ± 2.0
2.18	24.0 ± 0.20	24.6	258 ± 2.5
11.2	126 ± 1.3	29.7	274 ± 3.0
13.3	133 ± 1.2	32.1	290 ± 3.0

[a] $C^* = 2.3$ g L^{-1} for $L_p = 10^{-7}$ cm, 1.8 g L^{-1} for $L_p = 3 \times 10^{-7}$ cm, and 1.5 g L^{-1} for $L_p = 5 \times 10^{-7}$ cm.

Here, a is the length of a monomeric unit, l the contour length of the macromolecular chain, M_m the molar mass of a monomeric unit (in g mol^{-1}) and N_A Avogadro's constant. The total persistence length L_t is assumed to be the sum of the intrinsic part (L_p) and an electric part L_e. In the latter the value that applies when condensation occurs will be used ($\lambda \equiv Q/a > 1$)

$$L_t = L_p + L_e \simeq L_p + (4\kappa^2 Q)^{-1} \qquad (2)$$

The Bjerrrum length Q and the Debye–Hückel screening length κ^{-1} are defined by

$$Q = q^2/\epsilon k_B T \qquad (3)$$

$$\kappa^2 = 8\pi Q \mu \qquad (4)$$

with q the elementary charge, ϵ the relative permittivity of the solvent, $k_B T$ the thermal energy, and μ the ionic strength. As μ increases L_t/κ decreases and therefore c^* will increase. (See Table I of part 1 for estimates of C^*.)

Here again it has been found that the measured first cumulant follows the square-law dependence on $\sin^2(\theta/2)$ for $c > c^*$ (see Figure 1) but that with decreasing concentration, deviations occur from the highest angle on. In the latter case the initial slope of K_1 vs. $\sin^2(\theta/2)$ was used to calculate D_{eff}. The values of the diffusion coefficients for the systems investigated have been collected in Tables I–IV and are presented in Figure 2 in a log–log plot. As can be seen the concentration dependence of D_{eff} exhibits the same profile as found in part 1: at each value of c_s two distinct concentration regimes separated by a transition region can be observed. At very low concentration D_{eff} practically does not change with C but its value decreases with decreasing c_s as expected. In the semidilute regime D_{eff} increases with increasing polyelectrolyte concentration. The slope is approximately independent of c_s but at a given C the value of D_{eff} is the larger the smaller c_s.

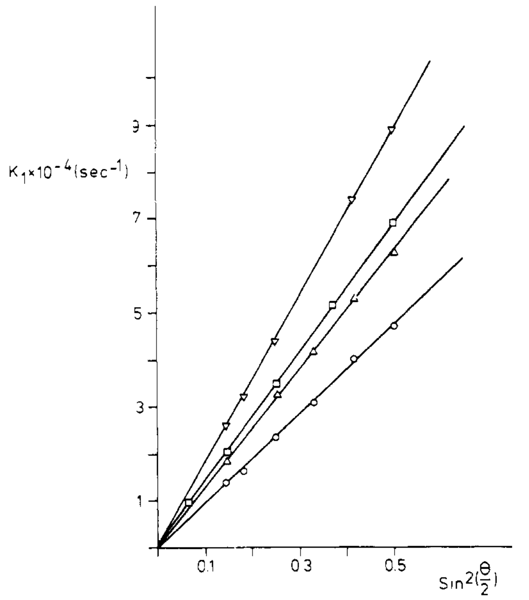

Figure 1. Dependence of the first cumulant K_1 (s^{-1}) on $\sin^2(\theta/2)$ for NaPSS ($M_w = 6.5 \times 10^5$ g mol^{-1}) at different polyelectrolyte and NaCl concentrations: (○) $C = 24.3$ g L^{-1}, $c_s = 0.1$ mol L^{-1}; (△) $C = 20.9$ g L^{-1}, $c_s = 0.05$ mol L^{-1}; (▽) $C = 17.3$ g L^{-1}, $c_s = 0.025$ mol L^{-1}; (□) $C = 6.98$ g L^{-1}, $c_s = 0.01$ mol L^{-1}.

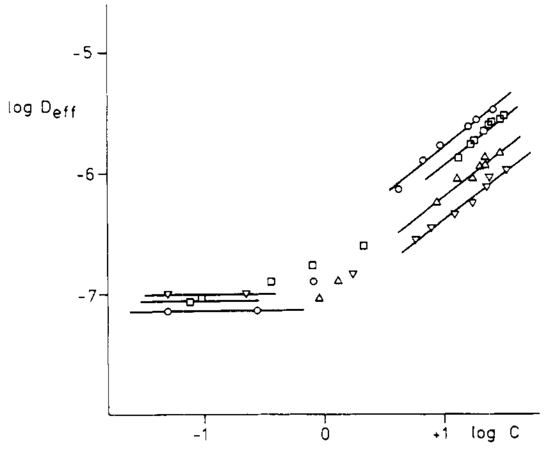

Figure 2. Variation of the effective diffusion coefficient D_{eff} (cm^2 s^{-1}) with macromolecular concentration C (g L^{-1}) for NaPSS ($M_w = 6.5 \times 10^5$ g mol^{-1}) at different NaCl concentrations: $c_s = 0.1$ (▽), 0.05 (△), 0.025 (□), and 0.01 mol L^{-1} (○).

Table IV
Effective Diffusion Coefficient of NaPSS ($M_w = 6.5 \times 10^5$ g mol^{-1}) in 0.01 MNaCl[a]

C, g/L	$10^8 D_{eff}$, cm^2/s	C, g/L	$10^8 D_{eff}$, cm^2/s
0.05	7.27 ± 0.07	9.65	171 ± 1.5
0.28	7.46 ± 0.07	16.2	246 ± 2.0
0.80	12.8 ± 0.10	19.6	277 ± 2.5
4.22	71.3 ± 0.7	26.4	333 ± 3
6.98	130 ± 1.0		

[a] $C^* = 1.4$ g L^{-1} for $L_p = 10^{-7}$ cm, 1.1 g L^{-1} for $L_p = 3 \times 10^{-7}$ cm, and 0.94 g L^{-1} for $L_p = 5 \times 10^{-7}$ cm.

Scaling theory predicts[2] that the effective diffusion coefficient should be inversely proportional to the correlation length ξ.

$$D_{eff} = \frac{k_B T}{\phi \eta \xi} = \frac{k_B T}{\phi \eta}(L_t/\kappa)^{1/4} a^{3/4} c^{3/4} \tag{5}$$

with c in monomolecules per unit volume.

In (5) ϕ is a hydrodynamic parameter (for simplicity often taken equal to 6π in analogy to Stokes' coefficient for a sphere without slip), η is the viscosity of the solvent, and the expression for ξ as proposed by Odijk[3] for wormlike, charged macromolecules has been used. According to (5), D_{eff} should decrease with increasing ionic strength, as $(L_t/\kappa)^{1/4}$ decreases with increasing μ. Therefore the experimental results are qualitatively in agreement with theory.

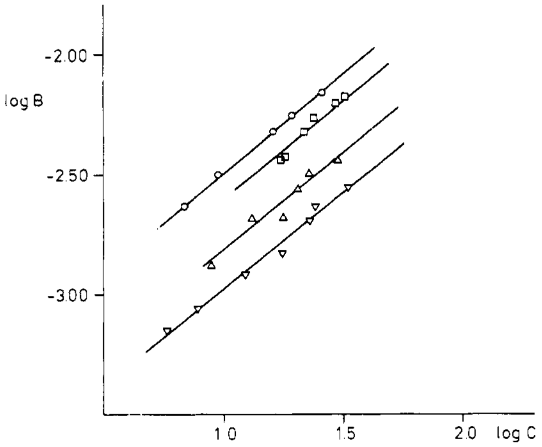

Figure 3. Variation of B (cm$^{3/2}$ s^{-1}) with macromolecular concentration C (g L^{-1}) for NaPSS ($M_w = 6.5 \times 10^5$ g mol^{-1}) in the semidilute regime (symbols same as in Figure 2), $L_p = 2 \times 10^{-7}$ cm.

It follows from the theoretical expression that the ionic strength dependence of D_{eff} is due only to the factor $(L_t/\kappa)^{1/4}$. Therefore the auxiliary quantity $B \equiv D_{eff}(\kappa/L_t)^{1/4}$ should be independent of ionic strength. As pointed out in part 1 two problems have to be faced in checking this prediction. The first refers to the value of L_p, which is not known accurately, and the other to the value of the ionic strength, in particular the contribution to μ from the counterions provided by the polyelectrolytes. The latter problem will only arise for relatively low values of c_s and large values of C. It has been proposed to use for μ the following expression based on a contribution of "noncondensed" counterions from the polyelectrolyte:

$$\mu = c_s\left[1 + \left(\frac{a}{Q}\right)\frac{c_m}{2c_s}\right] \qquad \lambda > 1 \tag{6}$$

where $c_m = C/M_m$ is the concentration of polyelectrolyte in monomol L^{-1}. It has been found in part 1 that the use of (6) and reasonable values for L_p ($10 \times 10^{-8} \le L_p \le 30 \times 10^{-8}$ cm) lead to values of B that, at constant c_s, are molar mass independent as required by theory. Values for B thus calculated are, however, still found to depend on c_s in a significant way if the values of D_{eff} derived from the light scattering experiments are used (see Figure 3). This seems to indicate that the theoretical expression for the diffusion coefficient in the semidilute regime, as given by (5), does *not* represent the complete dependence of D_{eff} on c_s.

It is possible to introduce in an empirical way an additional c_s dependence by assuming that ϕ in (5) is not a constant hydrodynamic parameter but a factor that varies with c_s. For each value of c_s, we calculate ϕ by solving for this factor expression (5), in which the theoretical exponent for ac, $^3/_4$, is replaced by an experimental one, ν, and the polymer concentration is expressed in g L^{-1}.

$$\phi = \frac{k_B T}{\eta}\frac{(L_t/\kappa)^{1/4}}{D_{eff}}\left(\frac{aN_A}{10^3 M_m}\right)^{\nu} C^{\nu} \tag{7}$$

Using a given value for L_p and a corresponding concentration exponent ν as found in part 1 (eventually slightly

Table V
Empirical Correction Factor $\overline{\phi}(c_s)$

		$\overline{\phi}(c_s)$		
c_s, mol L^{-1}	$M_w \times 10^{-5}$, g mol^{-1}	$L_p = 10^{-7}$ cm; $\nu = 0.83 \pm 0.02$	$L_p = 3 \times 10^{-7}$ cm; $\nu = 0.80 \pm 0.02$	$L_p = 5 \times 10^{-7}$ cm; $\nu = 0.79 \pm 0.02$
0.1	6.5	11.7 ± 0.7[a]	6.0 ± 0.4	5.5 ± 0.4
0.05	6.5	7.8 ± 0.6	4.2 ± 0.4	3.8 ± 0.3
0.025	6.5	4.7 ± 0.4	2.4 ± 0.1	2.2 ± 0.2
0.01	4.0	3.8 ± 0.1	1.93 ± 0.05	1.74 ± 0.04
0.01	6.5	3.73 ± 0.7	1.89 ± 0.04	1.70 ± 0.05
0.01	12.0	3.7 ± 0.2	1.89 ± 0.06	1.71 ± 0.03

[a] The standard deviation of the $\phi(c_s;C)$ with respect to the mean value.

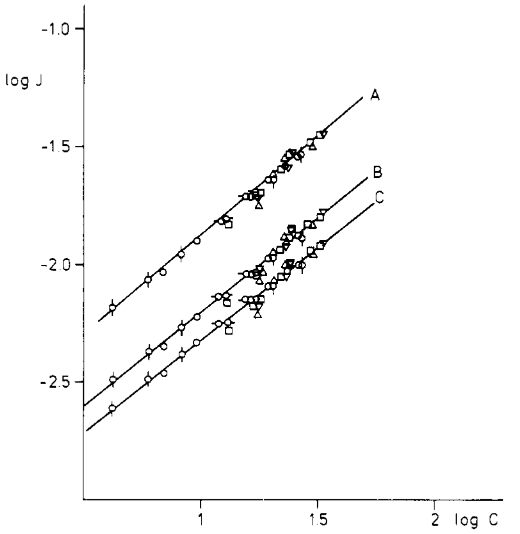

Figure 4. Variation of J (cm$^{3/2}$ s^{-1}) with macromolecular concentration C (g L^{-1}) for all NaPSS systems investigated in this paper and in part 1. A, B, and C correspond to values for L_p of 10^{-7}, 3×10^{-7}, and 5×10^{-7} cm, respectively. Symbols for $M_w = 6.5 \times 10^5$ g mol^{-1} as in Figures 2 and 3; for $M_w = 4 \times 10^5$ g mol^{-1}, $c_s = 0.01$ mol L^{-1} (○) and for $M_w = 1.2 \times 10^6$ g mol^{-1}, $c_s = 0.01$ mol L^{-1} (ϕ).

changed after a converging iteration), we find that ϕ is fairly constant within a given series of solutions with given c_s if (6) is applied for calculating μ.

Using the average values $\overline{\phi}(c_s)$ (see Table V), we find the auxiliary quantity $J \equiv B\overline{\phi}(c_s) = D_{\text{eff}}(\kappa/L_t)^{1/4}\overline{\phi}(c_s)$ to be only dependent on C, irrespective the value of c_s or M. In Figure 4, log J vs. log C has been presented for three different values of L_p, including the results of part 1. For all three least-squares lines the standard deviation of the J values with respect to the calculated line is 0.02–0.03. The slope, corresponding to the C exponent in J, is found, to lie within experimental uncertainty around 0.80 for the three values of L_p considered.

It thus seems that the effective diffusion coefficient of polyelectrolytes in salt solutions can be scaled in a proper way irrespective the molar mass and salt concentration. The theoretical predictions about the salt dependence of D_{eff}, as formulated by Odijk, are not in full agreement, however, with the experimental findings. It is not easy to trace the origin of the discrepancy between the experimental results and the theoretical approach, in particular because at constant salt concentration the theoretical expressions seem to be quite satisfactory (see part 1). Different possibilities can be envisaged.

One of them is a salt concentration dependence of the dynamical factor governing the relation between D_{eff} and the correlation length ξ. It is not impossible that this factor should depend on the nature of the solvent, which is the salt solution in the case of the systems considered. Hence it might show a salt concentration dependence. Such a salt effect should then by limited to dynamical quantities only and should therefore not be apparent for equilibrium properties such as the osmotic pressure. This will be investigated subsequently.

Another possibility would be a nonadequate salt concentration dependence in the theoretical expression of the Flory radius. According to the scaling approach, this quantity entirely determines the salt concentration dependence of the correlation length.

$$\xi \sim R_F(c^*/c)^{\nu} \simeq R_F^{1-3\nu} l^{\nu} a^{-\nu} c^{-\nu} \tag{8}$$

In the last member of (8) use has been made of the definition of c^*

$$c^* = (l/a)R_F^{-3} \tag{9}$$

In (8) and (9), c and c^* are expressed in monomoles per cm^3. If we assume $R_F \sim l^{\gamma}f(c_s)$, where $f(c_s)$ stands for the functional dependence of R_F on the salt concentration, it follows that

$$\xi \sim l^{\gamma(1-3\nu)+\nu} f^{1-3\nu} a^{-\nu} c^{-\nu} \tag{10}$$

The value of ν is fixed by the requirement that ξ should be independent of l (in the limit of large l) and therefore depends on γ. Odijk has proposed a theoretical expression for the Flory radius of a charged macromolecule in the presence of an excess of low molar mass salt.[3] It is based on a perturbation theory approach to the average dimension of the charged macromolecule treated as a wormlike chain.[5]

$$R_F = [\lim_{l\to\infty} \alpha_s^2 \langle S^2\rangle_0]^{1/2} = [(\lim_{l\to\infty} \alpha_s^2)\tfrac{1}{6} l L_t]^{1/2} \tag{11}$$

$$\lim_{l\to\infty} \alpha_s^2 \sim Z^{2/5} \tag{12}$$

Here, $\langle S^2\rangle_0$ stands for the unperturbed mean square radius of gyration of the wormlike chain with a total persistence length L_t and α_s is the expansion coefficient, which depends on the excluded volume parameter Z. The explicit expression for Z as used by Odijk, which involves a certain number of approximations, in particular, the assumption that only electrostatic interactions have to be taken into account to define the excluded volume, is given by

$$Z \sim \kappa^{-1} l^{1/2} L_t^{-3/2} \tag{13}$$

From (11)–(13) it follows that

$$R_F \sim l^{3/5}(L_t/\kappa)^{1/5} \tag{14}$$

so that $\gamma = {}^3/_5$ in this approach, leading to $\nu = {}^3/_4$. Under these conditions, (8) yields the expression for ξ, which has been used in (5) and which gives the salt concentration dependence of D_{eff} through the factor $(L_t/\kappa)^{1/4}$. As the power law of the macromolecular concentration of D_{eff} in the semidilute regime is determined in the same way and the theoretical power is only slightly smaller than what is found experimentally, the values of γ and ν are probably correct. It remains, however, that $f(c_s)$ may deviate from the value $(L_t/\kappa)^{1/5}$ in Odijk's expression (14), which is the result of a derivation involving a considerable number of assumptions not necessarily all justified for the systems considered. We shall discuss this in more detail after having ascertained whether or not the osmotic pressure of these solutions is correctly predicted by the theoretical approach based on scaling laws,[2] in particular, insofar as the salt concentration dependence is concerned.

Finally, it cannot be excluded that the value of the ionic strength, which is needed for evaluating the correction factor $(L_t/\kappa)^{1/4}$, is not correctly represented by (6), thus yielding an apparent discrepancy between the theoretical and the experimental salt concentration dependence of D_{eff}. We feel, however, that the assumptions underlying (6) cannot be primarily responsible for these discrepancies, as otherwise we would not have expected ϕ to be only slightly dependent on C irrespective the value of c_s.

It is also interesting to look at the salt concentration dependence of D_{eff} in the dilute regime. The hydrodynamic radius R_H of an isolated macromolecule can be obtained from D_{eff} at infinite dilution with respect to the macromolecular component

$$R_H = \lim_{C\to 0} \frac{k_B T}{6\pi\eta D_{\text{eff}}} \qquad (15)$$

and should be related to the root-mean-square radius of gyration $\langle S^2\rangle^{1/2}$. The latter can be evaluated theoretically by using the theory of Odijk and Houwaart[5] in combination with the Fixman–Skolnick expression for the electrostatic excluded volume[6] (see part 1). As pointed out before, if not enough values are available at low concentrations to perform a proper extrapolation to $C = 0$, an approximate value for the hydrodynamic radius R_H' may be obtained by using D_{eff} at the lowest concentration at which measurements have been performed.

We have calculated the value of R_H' for the three salt concentrations 0.1, 0.025, and 0.01. This yields a ratio of 1:1.17:1.36, which may be compared to the ratio of the theoretical expression for $\langle S^2\rangle^{1/2}$ under the same conditions. Using again three estimates for L_p, namely, 1×10^{-7}, 3×10^{-7}, and 5×10^{-7} cm, respectively, we find the following ratios: 1:1.34:1.70, 1:1.24:1.49, and 1:1.20:1.41. It is difficult to conclude anything definite at this stage about the theoretical salt concentration dependence of the root-mean-square radius of gyration although the comparison is not too unsatisfactory. This is in part due to the uncertainty about the value of L_p and to the known fact that R_H may differ from $\langle S^2\rangle^{1/2}$.

Conclusions

It seems from the combination of the results presented here and in part 1 that the conclusions of scaling theory for polyelectrolyte–salt solutions are, at least qualitatively, justified by the experimental results obtained from quasi-elastic light scattering experiments on the NaPSS–NaCl system. There is still some doubt about the exact concentration power law for the correlation length in the semidilute regime in relation to the uncertainty about the exact value of the intrinsic persistence length of the poly(styrenesulfonate) chain. It is clear that the exponent is slightly larger than the theoretical value $^3/_4$ and may be even closer to $^4/_5$. The results obtained at different salt concentrations have revealed that the dependence of the effective diffusion coefficient in the semidilute regime is *not* fully accounted for by the theoretical expressions.

Registry No. NaPSS, 9080-79-9; NaCl, 7647-14-5.

References and Notes

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Scaling Relations for Aqueous Polyelectrolyte–Salt Solutions. 3. Osmotic Pressure as a Function of Molar Mass and Ionic Strength in the Semidilute Regime

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ABSTRACT: The osmotic pressure of aqueous solutions of sodium poly(styrenesulfonate) in NaCl of various concentrations c_s has been measured as a function of the macromolecular concentration C for three different molar masses. In the semidilute regime it has been found that at constant c_s the osmotic pressure increases with increasing C according to a power law with an exponent that is close to the value predicted by the scaling theory for polyelectrolyte solutions in the presence of excess salt. Also the theoretical requirement that in the semidilute regime osmotic pressure should be independent of molar mass has been found to be satisfied. The change of the osmotic pressure with salt concentration shows the same kind of discrepancy with respect to theory as observed with the effective diffusion coefficient in the semidilute regime measured with the help of quasi-elastic light scattering. These discrepancies may be understood if it is assumed that the effect of the low molar mass electrolyte not only is limited to screening of the electrostatic interactions in solution but also affects the quality of the polyelectrolyte solvent. With increasing salt concentration the water–salt mixture no longer acts as an athermal solvent.

Introduction

In two previous papers,[1,2] to be called parts 1 and 2 respectively, quasi-elastic light scattering experiments on aqueous solutions of sodium poly(styrenesulfonate) (NaPSS) of different molar masses and with different concentrations of added NaCl have been reported. In part 1 it has been shown that in the semidilute regime the measured diffusion coefficient D_{eff} of the charged macromolecule at constant salt concentration increases with macromolecular concentration according to a power law that is close to the predictions of scaling theory for polyelectrolytes[3] if D_{eff} is assumed to be inversely proportional to the correlation length ξ. Moreover, D_{eff} was found to be molar mass independent in the semidilute concentration region, in agreement with theoretical predictions. Experiments performed at different concentrations c_s of

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