

# Dynamic Light Scattering of Flexible Highly Charged Polyelectrolytes at Infinite Dilution

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Literature data on the diffusion behavior at infinite dilution, as measured with dynamic light scattering, of flexible highly charged polyelectrolytes were collected. The apparent diffusion coefficients extrapolated to zero polyelectrolyte concentration were investigated for different molar masses and ionic strengths. The experimental values were compared with theoretical  $D_0$  values calculated with a theoretical procedure based on the wormlike chain model of Yamakawa and Fujii for the translational friction coefficient. The electrostatic persistence length according to Le Bret and the excluded volume theory of Fixman and Skolnick were applied. With the hydrodynamic expansion factor of Barrett and the counterion condensation theory of Manning, satisfactory agreements were found for  $D_0$  values measured at moderate and low ionic strengths. Significant deviations occur at high ionic strength (3.1 M). For flexible polyelectrolytes in the ionic strength range from 0.001 up to 0.5 M the ionic strength dependence of the electrostatic persistence length shows a scaling behavior close to  $\kappa^{-1}$ . The electrostatic persistence length appears to be molar mass independent.

## Introduction

Dynamic light scattering is an excellent tool to study the dynamics of polyelectrolyte chains in dilute solutions. From the intensity autocorrelation function of the scattered light an apparent diffusion coefficient can be obtained. In dilute polyelectrolyte solutions with added low molar mass salt the apparent diffusion coefficient is a linear function of the polyelectrolyte concentration.<sup>1–3</sup> The apparent diffusion coefficient extrapolated to zero polyelectrolyte concentration represents the dynamics of an average single polyelectrolyte chain.

From a physical point of view polyelectrolytes can be distinguished in two major groups: stiff and flexible polyelectrolytes. Polyelectrolytes are called stiff when their intrinsic persistence length is large (e.g., DNA). Flexible polyelectrolytes are characterized by a small intrinsic persistence length (e.g., NaPSS). In polyelectrolyte theory<sup>4</sup> the total persistence length is the sum of the intrinsic persistence length and the electrostatic persistence length. The intrinsic persistence length represents the stiffness of the uncharged chain. The electrostatic persistence length is due to the electric charges on the chain. Several theories<sup>4–6</sup> were developed to calculate the electrostatic persistence length.

The conformation of a flexible polyelectrolyte can be changed by varying the added low molar mass salt. The addition of low molar mass salt results in the screening of the electric charges on the polyion. Short-range electrostatic interactions are incorporated in the electrostatic persistence length while long range electrostatic interactions are involved in the excluded volume. The number of effective charges on the chain can be smaller than the nominal number of fixed charges on the chain due to counterion condensation.<sup>7</sup>

Several researchers<sup>1–3,8–10</sup> have reported apparent diffusion coefficients extrapolated to zero polyelectrolyte concentration of flexible highly charged polyelectrolytes.

In this study a theoretical procedure based on a wormlike chain model of Yamakawa and Fujii is applied on many values for the apparent diffusion coefficient at infinite dilution found in the recent literature. The electrostatic persistence length

according to Le Bret, the excluded volume theory of Fixman and Skolnick, the counterion condensation theory of Manning, and the hydrodynamic expansion factor of Barrett were incorporated in the theoretical procedure. The apparent diffusion coefficients at infinite dilution of the flexible polyelectrolytes sodium poly(styrenesulfonate) (NaPSS) and linear poly(ethyl-enimine) (LPEI) were collected for different chain lengths and ionic strengths.

## Results and Discussion

In dynamic light-scattering studies on dilute polyelectrolyte solutions,<sup>1–3</sup> it is observed that the apparent diffusion coefficient is a linear function of the polyelectrolyte concentration. The apparent diffusion coefficient at infinite dilution can be obtained by extrapolating the linear least-squares best fit of the apparent diffusion coefficient versus the polyelectrolyte concentration to zero polyelectrolyte concentration. In this paper many literature data for the apparent diffusion coefficient at infinite dilution  $D_0$  of two flexible polyelectrolytes are collected. The polyelectrolytes are NaPSS and LPEI. A theoretical procedure to calculate  $D_0$  is given, and the experimental  $D_0$  values are compared with theoretical  $D_0$  values.

In the following section a theoretical procedure is given to calculate a theoretical diffusion coefficient at infinite dilution. The Einstein relation gives the relationship between the diffusion coefficient at infinite dilution  $D_0$  and the friction coefficient  $f$  as

$$D_0 = \frac{k_b T}{f} \quad (1)$$

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

$$f = \alpha_h f_0 \quad (2)$$

with  $f_0$  the friction coefficient without excluded volume and  $\alpha_h$  the hydrodynamic expansion factor. Yamakawa and Fujii<sup>11</sup> have derived a procedure to calculate the translational friction coefficient of a wormlike chain of finite thickness without

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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  $N_k > 2.278$

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

and for  $N_k \leq 2.278$

$$\begin{aligned} \frac{3\pi\eta_0 L}{f_0} = & C_1 \ln\left(\frac{N_k}{d}\right) + C_2 + C_3 N_k + C_4 N_k^2 + C_5 N_k^3 + \\ & C_6 \left(\frac{d}{N_k}\right) \ln\left(\frac{N_k}{d}\right) + C_7 \left(\frac{d}{N_k}\right) + C_8 \left(\frac{d}{N_k}\right)^2 + C_9 \left(\frac{d}{N_k}\right)^3 + C_{10} \left(\frac{d}{N_k}\right)^4 \end{aligned} \quad (4)$$

with  $\eta_0$  the viscosity of the solvent. The coefficients  $A_1 \dots A_5$  and  $C_1 \dots C_{10}$ , which are functions of the reduced diameter  $d = r/L_t$ , are given in ref 11. The number of Kuhn lengths  $N_k = L/2L_t$ , with  $L_t$  being the total persistence length.

In eq 2  $\alpha_h$  is the hydrodynamic expansion factor which depends on the excluded volume parameter  $z$

$$z = \frac{3^{3/2}}{32\pi^{3/2}} \beta L^{1/2} L_t^{-7/2} \quad (5)$$

The excluded volume  $\beta$  between Kuhn segments with length  $2L_t$  is approximated as  $\beta = \beta_0 + \beta_e$ , where  $\beta_0$  represents hard-core interactions and  $\beta_e$  electrostatic interactions. The hard-core part<sup>12</sup> is given by  $\beta_0 = 4\pi L_t^2 r$ , with  $r$  being the radius of a rod segment. Fixman and Skolnick<sup>13</sup> have calculated for the binary cluster integral  $\beta_e$

$$\beta_e \approx 8L_t^2 \kappa^{-1} R(\omega) \quad (6)$$

where  $R(\omega)$  is given as

$$R(\omega) = \int_0^{\pi/2} \sin^2 \theta \int_0^{\omega/\sin \theta} x^{-1} (1 - e^{-x}) dx d\theta \quad (7)$$

with Manning's counterion condensation<sup>7</sup>  $\omega = (2\pi/Q)\kappa^{-1}e^{-2\kappa r}$ . In eq 6,  $\kappa^{-1}$  is the Debye–Hückel screening length. The Bjerrum length  $Q = 7.135 \text{ \AA}$  for water at 25 °C. To calculate the expansion factor  $\alpha_h$ , we can use the Barrett equation<sup>14</sup>

$$\alpha_h = (1 + 6.09z + 3.59z^2)^{0.1} \quad (8)$$

To calculate theoretical  $D_0$  values, values for the total persistence lengths and a value for the radius  $r$  of the polyion are needed. For polyelectrolytes the total persistence length,  $L_t$  is written as<sup>4</sup>

$$L_t = L_0 + L_e \quad (9)$$

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. The preceding theoretical procedure was also presented in our earlier studies.<sup>2,3</sup>

The electrostatic persistence length for a line charge has been derived by Odijk<sup>4</sup> and Skolnick and Fixman<sup>5</sup> (OSF) on the basis of a linearized form of the Poisson–Boltzmann equation. Another calculation for the electrostatic persistence length was

**TABLE 1: Comparison between Experimental and Theoretical  $D_0$  Values of NaPSS with  $M_w = 77.4 \text{ kg/mol}$  without and with Excluded Volume and the Total Persistence Length According to Le Bret for Five Ionic Strengths**

$c_s$ (M)	$D_0^{\text{exptl}}$ ( $10^{-11} \text{ m}^2/\text{s}$ ) <sup>a</sup>	$L_t$ (Å) <sup>b</sup>	$D_0$ ( $10^{-11} \text{ m}^2/\text{s}$ ) <sup>c</sup>	$D_0$ ( $10^{-11} \text{ m}^2/\text{s}$ ) <sup>d</sup>
0.01	$2.36 \pm 0.07$	66.0	3.05	2.33
0.02	$2.52 \pm 0.05$	48.5	3.31	2.52
0.05	$2.59 \pm 0.01$	33.7	3.70	2.83
0.1	$2.85 \pm 0.02$	26.6	3.99	3.09
0.5	$3.09 \pm 0.003$	17.9	4.48	3.40

<sup>a</sup>Data reported by Tanahatue and Kuil.<sup>2</sup> <sup>b</sup>Calculated with  $L_0 = 12 \text{ \AA}$ . <sup>c</sup>Calculated without excluded volume. <sup>d</sup>Calculated with excluded volume.

given by Le Bret.<sup>6</sup> For a toroid he applied a numerical procedure on the basis of the complete Poisson–Boltzmann equation. The electrostatic persistence length is given in Tables 1 and 2 of ref 6 as a function of the charge parameter, the polyion radius, and the Debye–Hückel screening length. The data in his Tables 1 and 2 are calculated for a polyion radius of  $10 \text{ \AA}$ . For other values of the polyion radius the electrostatic persistence length can be calculated. The charge parameter is set to unity since Manning's counterion condensation theory is assumed.

Our theoretical procedure views the polyelectrolyte as a wormlike chain and takes into account for the finite thickness of the chain. Therefore the OSF electrostatic persistence length calculation can not be applied since the OSF electrostatic persistence length has been derived for a line charge. The electrostatic persistence length calculation according to Le Bret is used in all our calculations.

The data for two flexible polyelectrolytes were taken from the literature. The polyelectrolytes are sodium poly(styrenesulfonate) and linear poly(ethylenimine). The radius of the polyelectrolyte sodium poly(styrenesulfonate) is set to  $9 \text{ \AA}$ . This value is an estimation of the bond lengths and angles in NaPSS and takes into account a possible layer of immobile water molecules or counterions around the polyelectrolyte chain. For the monomer contour distance a value of  $2.5 \text{ \AA}$  is taken, based on the bondlengths and angles of the monomer. For the polyelectrolyte linear poly(ethylenimine), the radius is set to  $3 \text{ \AA}$  and for the monomer contour distance a value of  $3.5 \text{ \AA}$  is taken.<sup>1</sup>

The electrostatic persistence lengths according to Le Bret were calculated for a polyion radius of  $9 \text{ \AA}$  in the ionic strength range from about 0.001 up to 1.5 M with the charge parameter set to unity. The obtained electrostatic persistence length as a function of the ionic strength follows in the chosen ionic strength range a power law  $L_e \propto c_s^{-0.6}$ , close to  $\kappa^{-1}$  scaling of  $L_e$ . From interpolation, the electrostatic persistence lengths of NaPSS at the measured ionic strengths were obtained. For linear poly(ethylenimine) the same procedure as described above was applied but now for a polyion radius of  $3 \text{ \AA}$ . The ionic strength range reaches from 0.01 up to about 1 M. In this case the same proportionality  $L_e \propto c_s^{-0.6}$  was obtained.

For the intrinsic persistence length of NaPSS a value of  $12 \text{ \AA}$ <sup>15,16</sup> is used. The intrinsic persistence length of linear poly(ethylenimine)<sup>1</sup> is assumed to be  $5 \text{ \AA}$ .

In Tables 1 and 2 theoretically calculated  $D_0$  values and experimentally obtained  $D_0$  values of NaPSS from our previous studies<sup>2,3</sup> are collected for different ionic strengths and molar masses. The temperature was 25 °C. When the radius is changed between 8 and  $10 \text{ \AA}$ , a change in the theoretical  $D_0$  value of about 3% is found. The calculated  $D_0$  values without taking into account for the excluded volume effect are larger

**TABLE 2: Comparison between Experimental and Theoretical  $D_0$  Values of NaPSS without and with Excluded Volume and the Total Persistence Length According to Le Bret for Five Molar Masses at  $c_s = 0.1$  M NaCl**

$M_w$ (kg/mol)	$D_0^{\text{exptl}}$ ( $10^{-11}$ m <sup>2</sup> /s) <sup>a</sup>	$L_t$ (Å) <sup>b</sup>	$D_0$ ( $10^{-11}$ m <sup>2</sup> /s) <sup>c</sup>	$D_0$ ( $10^{-11}$ m <sup>2</sup> /s) <sup>d</sup>
46.4	4.14 ± 0.08	26.6	5.16	4.12
77.4	2.85 ± 0.02	26.6	3.99	3.09
123	2.01 ± 0.03	26.6	3.17	2.37
168	1.75 ± 0.02	26.6	2.71	1.98
350	1.21 ± 0.01	26.6	1.88	1.30

<sup>a</sup>Data reported by Tanahatoo and Kuil.<sup>3</sup> <sup>b</sup>Calculated with  $L_0 = 12$  Å. <sup>c</sup>Calculated without excluded volume. <sup>d</sup>Calculated with excluded volume.

**TABLE 3: Comparison between Experimental and Theoretical  $D_0$  Values of NaPSS with  $M_w = 1000$  kg/mol without and with Excluded Volume and the Total Persistence Length According to Le Bret for Six Ionic Strengths**

$c_s$ (M)	$D_0^{\text{exptl}}$ ( $10^{-12}$ m <sup>2</sup> /s) <sup>a</sup>	$L_t$ (Å) <sup>b</sup>	$D_0$ ( $10^{-12}$ m <sup>2</sup> /s) <sup>c</sup>	$D_0$ ( $10^{-12}$ m <sup>2</sup> /s) <sup>d</sup>
0.001	3.2	211.8	4.2	2.8
0.004	3.6	103.1	5.5	3.5
0.01	4.2	66.2	6.6	4.1
0.05	5.4	33.8	8.8	5.5
0.1	7.5	26.7	9.7	6.2
0.5	9.4	17.9	11.3	7.0

<sup>a</sup>Data reported by Borochov and Eisenberg.<sup>10</sup> <sup>b</sup>Calculated with  $L_0 = 12$  Å. <sup>c</sup>Calculated without excluded volume. <sup>d</sup>Calculated with excluded volume.

**TABLE 4: Comparison between Experimental and Theoretical  $D_0$  Values of NaPSS without and with Excluded Volume and the Total Persistence Length according to Le Bret for Different Molar Masses at  $c_s = 0.002$  M Na<sub>3</sub>PO<sub>4</sub>**

$M_w$ (kg/mol)	$D_0^{\text{exptl}}$ ( $10^{-11}$ m <sup>2</sup> /s) <sup>a</sup>	$L_t$ (Å) <sup>b</sup>	$D_0$ ( $10^{-11}$ m <sup>2</sup> /s) <sup>c</sup>	$D_0$ ( $10^{-11}$ m <sup>2</sup> /s) <sup>d</sup>
25.4	5.9 ± 0.2	60.7	6.0	4.9
40.7	5.1 ± 0.4	60.7	4.5	3.6
57.9	3.5 ± 0.2	60.7	3.7	2.9
177	1.62 ± 0.06	60.7	1.96	1.41
354	1.01 ± 0.07	60.7	1.35	0.92
690	0.72 ± 0.06	60.7	0.94	0.61
1060	0.52 ± 0.04	60.7	0.75	0.47

<sup>a</sup>Data reported by Wang and Yu.<sup>8</sup> <sup>b</sup>Calculated with  $L_0 = 12$  Å. <sup>c</sup>Calculated without excluded volume. <sup>d</sup>Calculated with excluded volume.

than the experimental  $D_0$  values. When the excluded volume correction is applied, the theoretical values approach the experimental values very closely. At our lowest ionic strengths the agreement is remarkable. At high ionic strengths the deviation is about 10%.

In Table 3, experimental data of Borochov and Eisenberg<sup>10</sup> and theoretical data calculated with our theoretical procedure are given for NaPSS with a molar mass of 1000 kg/mol. The experiments were performed at a temperature of 20 °C. Again a remarkable agreement is seen except for the highest ionic strengths where the deviation is about 20%.

Tables 4–6 contain literature data by Wang and Yu<sup>8</sup> for NaPSS at a temperature of 25 °C for many molar masses at three different ionic strengths. Since not all added salts are 1–1 salts and some phosphates were added, the ionic strength is calculated as  $(1/2)\sum_i\{c_i Z_i^2\}$  with  $i$  being the number of different ions in the solution and  $c_i$  and  $Z_i$  the molar concentration and charge of the  $i$ th ion respectively. Tables 4 and 5 show a satisfactory agreement between the experimental and theoretical  $D_0$  values. The experimental  $D_0$  values in Table 4 are values

**TABLE 5: Comparison between Experimental and Theoretical  $D_0$  Values of NaPSS without and with Excluded Volume and the Total Persistence Length According to Le Bret for Different Molar Masses at  $c_s = 0.15$  M NaCl and 8 mM Phosphates**

$M_w$ (kg/mol)	$D_0^{\text{exptl}}$ ( $10^{-11}$ m <sup>2</sup> /s) <sup>a</sup>	$L_t$ (Å) <sup>b</sup>	$D_0$ ( $10^{-11}$ m <sup>2</sup> /s) <sup>c</sup>	$D_0$ ( $10^{-11}$ m <sup>2</sup> /s) <sup>d</sup>
25.4	6.5 ± 0.2	21.9	7.3	6.0
40.7	5.0 ± 0.2	21.9	5.8	4.7
57.9	3.9 ± 0.1	21.9	4.9	3.9
146	2.19 ± 0.06	21.9	3.12	2.31
177	2.13 ± 0.06	21.9	2.83	2.07
215	1.99 ± 0.08	21.9	2.58	1.86
354	1.31 ± 0.06	21.9	2.01	1.40
690	0.92 ± 0.01	21.9	1.45	0.95
1060	0.69 ± 0.03	21.9	1.17	0.74

<sup>a</sup>Data reported by Wang and Yu.<sup>8</sup> <sup>b</sup>Calculated with  $L_0 = 12$  Å. <sup>c</sup>Calculated without excluded volume. <sup>d</sup>Calculated with excluded volume.

**TABLE 6: Comparison between Experimental and Theoretical  $D_0$  Values of NaPSS without and with Excluded Volume and the Total Persistence Length According to Le Bret for Different Molar Masses at  $c_s = 3.1$  M KCl and 8 mM Phosphates**

$M_w$ (kg/mol)	$D_0^{\text{exptl}}$ ( $10^{-11}$ m <sup>2</sup> /s) <sup>a</sup>	$L_t$ (Å) <sup>b</sup>	$D_0$ ( $10^{-11}$ m <sup>2</sup> /s) <sup>c</sup>	$D_0$ ( $10^{-11}$ m <sup>2</sup> /s) <sup>d</sup>
25.4	9.7 ± 0.3	14.1	8.5	6.6
40.7	7.4 ± 0.2	14.1	6.9	5.2
57.9	6.4 ± 0.1	14.1	5.9	4.3
146	3.7 ± 0.1	14.1	3.8	2.6
177	3.84 ± 0.03	14.1	3.46	2.35
354	2.63 ± 0.05	14.1	2.48	1.59
690	2.00 ± 0.04	14.1	1.80	1.09
1060	1.40 ± 0.04	14.1	1.46	0.85

<sup>a</sup>Data reported by Wang and Yu.<sup>8</sup> <sup>b</sup>Calculated with  $L_0 = 12$  Å. <sup>c</sup>Calculated without excluded volume. <sup>d</sup>Calculated with excluded volume.

**TABLE 7: Comparison between Experimental and Theoretical  $D_0$  Values of LPEI without and with Excluded Volume and the Total Persistence Length According to Le Bret for Two Molar Masses at Different Ionic Strengths**

$c_s$ (M)	$D_0^{\text{exptl}}$ ( $10^{-11}$ m <sup>2</sup> /s) <sup>a</sup>	$L_t$ (Å) <sup>b</sup>	$D_0$ ( $10^{-11}$ m <sup>2</sup> /s) <sup>c</sup>	$D_0$ ( $10^{-11}$ m <sup>2</sup> /s) <sup>d</sup>
$M_w = 41.5$ (kg/mol)				
0.01	1.39 ± 0.12	27.0	3.18	1.86
0.025	1.92 ± 0.10	17.7	3.73	2.16
0.1	2.48 ± 0.06	10.5	4.60	2.72
$M_w = 88.2$ (kg/mol)				
0.025	1.12 ± 0.05	17.7	2.52	1.36

<sup>a</sup>Data reported by Smits et al.<sup>1</sup> <sup>b</sup>Calculated with  $L_0 = 5$  Å. <sup>c</sup>Calculated without excluded volume. <sup>d</sup>Calculated with excluded volume.

determined at low polyelectrolyte concentrations and are not extrapolated values. The data at very high ionic strength (3.1 M) collected in Table 6 show relatively large deviations. The deviation is on average about 30% for the four lowest molar masses and is on average about 40% for the four highest molar masses.

Data reported by Smits et al.<sup>1</sup> for linear poly(ethylenimine) are collected in Table 7. The temperature was 25 °C. Again a fair agreement between experimental and theoretical data is seen. When the radius is changed by 1 Å the theoretical  $D_0$  value varies about 3%.

The collected data show a remarkable agreement between experimental and theoretical apparent diffusion coefficients at infinite dilution in the ionic strength range from 0.001 up to 0.5 M. For different molar masses, ionic strengths, and two

different flexible polyelectrolytes, the theoretical procedure predicts the experimental  $D_0$  values very well.

Some interesting remarks can be made for the electrostatic persistence length. It appears that the data can be described by assuming a molar mass independent electrostatic persistence length. Secondly, the ionic strength dependence of the electrostatic persistence length shows a scaling behavior close to  $\kappa^{-1}$  in the ionic strength range from 0.001 up to 0.5 M. These results are based on the preceding interpretation of  $D_0$  values for two flexible polyelectrolytes with a rather different chemical structure and takes important conceptions such as the electrostatic persistence length, the electrostatic excluded volume and counterion condensation into account.

The flexible polyelectrolytes studied can be modeled as wormlike chains consisting of rodlike segments with length  $2L_t$  and radius  $r$  in a wide ionic strength range. It is possible that this model can not be applied when the segments are not rodlike. This occurs when the total persistence length becomes small. The excluded volume  $\beta$  is valid for  $L_t \gg r$ . As the ionic strength increases the validity of this condition becomes questionable. This could be the reason for the relatively large deviation between the experimental and theoretical  $D_0$  values in Table 6 at 3.1 M.

Secondly, it is possible that the amount of condensed counterions depends on the length of the rodlike chain segment. It must be noted that the application of the counterion condensation theory of Manning is only valid for infinitely long rods. When the ionic strength increases, the total persistence length decreases and the chain segment length decreases while the number of chain segments increases. The amount of condensed counterions will decrease and the effective linear charge density will increase.

These two preceding phenomena occur simultaneously due to decreasing segment length and increasing number of segments as the ionic strength increases. Nevertheless, taking into account the high ionic strength of 3.1 M compared to the ionic strength range from 0.001 up to 0.5 M and the forementioned drawbacks of the theoretical procedure at high ionic strength, the theoretical  $D_0$  values at 3.1 M should be considered in reasonable agreement.

## Conclusions

The wormlike chain model of Yamakawa and Fujii for the translational friction coefficient, including the electrostatic persistence length of Le Bret; the excluded volume theory of Fixman and Skolnick, as well as Barrett; and the counterion condensation theory of Manning; can be used successfully to interpret experimental apparent diffusion coefficients at infinite dilution. This conclusion is based on the comparison with experimental  $D_0$  values of two different flexible polyelectrolytes, sodium poly(styrenesulfonate), and linear poly(ethylenimine) in the ionic strength range from 0.001 up to 0.5 M. At very high ionic strength (3.1 M) the deviations between experimental and theoretical data become relatively large.

The ionic strength dependence of the electrostatic persistence length shows a scaling behavior close to  $\kappa^{-1}$ . The electrostatic persistence length appears to be molar mass independent.

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