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Comparison of Experimental and Theoretical Persistence Length of Some Polyelectrolytes at Various Ionic Strengths

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ABSTRACT: The literature values of the intrinsic viscosity–molecular weight dependence of some polyelectrolytes have been analyzed on the basis of Yamakawa's theory in order to derive the persistence length q with a computer fitting procedure. Sodium polyacrylate, poly(styrenesulfonate), poly[((acrylamido)methyl)propanesulfonate], (carboxymethyl)cellulose, and the sodium salt of an isobutyl vinyl ether–maleic anhydride copolymer have been investigated in the 1.0–0.005 M ionic strength range. The persistence lengths l_p, determined by extrapolation to infinite ionic strength with a linear q vs. $I^{-1/2}$ plot, agreed with those of the corresponding uncharged polymers. In addition, the q values of the vinylic polyelectrolytes appeared to extrapolate toward a similar value, about 500 Å, at infinite dilution, indicating a high degree of rigidity. The observed $I^{-1/2}$ dependence of the electrostatic contribution to the persistence length l_e differed from the I^{-1} dependence predicted in the Odijk–Skolnick–Fixman theory and agreed, at least semiquantitatively, with that calculated from the recent treatments of Le Bret and Fixman. The influence of the ionization degree on the persistence length of sodium polyacrylate was also studied.

Introduction

During the past 5 years, several attempts have been made to theoretically express the persistence length of polyelectrolytes as a function of ionic strength in order to obtain an experimental value of this parameter from the molecular weight dependences of hydrodynamic data (intrinsic viscosity, radius of gyration). Since the persistence length, equal to half the Kuhn statistical segment, is a measure of how far a polymeric chain persists in a given direction, it really defines the chain rigidity. In the particular case of polyelectrolytes, the persistence length is a sum of two contributions: a bare persistence length l_p due to the rigidity of the chain backbone and an electrostatic persistence lenth l_e arising from the repulsion between neighboring ionic sites, the latter being markedly dependent upon the concentration of added salt. Theoretical estimation of l_e has been achieved by Odijk,[1-4] Skolnick and Fixman,[5] and recently by Fixman[6] and Le Bret.[7,8]

Presently, the most commonly used relationship for the determination of the persistence length from viscosity results is that established for the case of wormlike chains

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Table I
Experimental Molecular Weight–Viscosity Relationships, Persistence Length, and Diameter Obtained by the Procedure of Yamakawa and Fujii for Sodium Polyacrylate and Sodium Poly(styrenesulfonate)

		lit. values			calcd values		
polyelectrolyte (ref)	I, mol·L^{-1}	$K \times 10^4$, dL·g^{-1}	ν	M range, M_0, and h	q, Å	d, Å	$Y \times 10^3$
sodium polyacrylate (19) (NaBr, 15 °C)	0.0025	2.49	0.89	$M = 1.5 \times 10^4$ to 5×10^5, $M_0 = 94$, $h = 2.5$ Å	182	6.3	6
	0.005	4.42	0.83		158	6.7	13
	0.01	1.36	0.89		115	3.9	20
	0.025	1.63	0.84		100	(0.7)	23
	0.05	2.81	0.77		65	1.3	10
	0.1	2.54	0.755		44	2.5	3
	0.5	5.27	0.628		21	4.0	6
	1.5	12.4	0.50		12	4.2	4
sodium polyacrylate (18) (NaBr, 25 °C)	0.01	1.32	0.910	$M = 0.9 \times 10^4$ to 8×10^5	135	3.8	21
	0.025	1.76	0.850		90	2.9	10
	0.1	3.12	0.755		51	3.5	7
	0.5	5.06	0.656		25	5.2	4
sodium poly(styrenesulfonate) (20)	0.005	0.23	0.93	$M = 3.9 \times 10^5$ to 23×10^5, $M_0 = 206$, $h = 2.5$ Å	136	3.4	5
	0.01	0.28	0.89		104		4
	0.02	1.01	0.78		74	8.4	2
	0.05	1.39	0.72		49	8.3	1
	0.1	1.78	0.68		38	8.3	1
	0.5	1.86	0.64		26	6.3	0.7

by Yamakawa and Fujii,[9,10] starting with a Kratky–Porod chain model. This treatment was recently applied to polyamides[11] and cellulose derivatives[12] and also to polyelectrolytes at various ionic strengths: sodium polyacrylate (PAANa),[13] sodium poly[((acrylamido)methyl)propanesulfonate] (PAMPSNa),[14] and the sodium salt of an alternating copolymer of isobutyl vinyl ether and maleic anhydride (PBVMANa) at various degrees of neutralization.[15] For the PAMPSNa, the experimental persistence length value q, obtained from viscosity data, is in fairly good agreement with that estimated according to Benoit and Doty[16] from the radius of gyration measured by light scattering. For PAANa and PBVMANa, the persistence length has been found to depend linearly upon the inverse of the root square of the ionic strength in the range 0.01–1.0 M.

The determination of the viscosity of polyelectrolytes has always appeared to be very difficult at low ionic strength, owing to the expansion of the polyions as the ionic strength and/or the concentration decreases. Any attempt to investigate the viscometric behavior of polyions at very low ionic strength leads to inconsistent results. In a study of the viscosity of sodium (carboxymethyl)cellulose (CMCNa) at very low gradient, Vink observed that, in the low molecular weight range, the experimental viscosity of the polyions in pure water is much higher than the calculated viscosity of neutral rodlike molecules of equal size.[17] Such a difference is certainly due to the electroviscous effect, i.e., the difference of motion of the polyion with respect to its counterionic atmosphere. Therefore the use of the viscometric experiments for the determination of conformational parameters, and in particular the persistence length, of polyions is restricted to a relatively high ionic strength range (0.005–1.0 M). Otherwise, for $I <$ 0.005 M, the persistence length can be obtained from the rotatory diffusion coefficient measured by the relaxation time of the birefringence or the frequency dispersion of the dielectric increment. The application of an electric field to a conducting medium as short pulses of high voltage (electrooptical methods) or as a sinusoidal field of low voltage (dielectric methods) can only be performed at very low ionic strengths (10^{-3}–10^{-6} M). This is the reason why the use of these methods to investigate the conformation of polyions is, on the contrary, limited to the low ionic strength range. It thus seems to be impossible to find a single experimental method for continuously following the conformational change of a polyion over the whole ionic strength range.

The purpose of the present work is to gain a better insight into the ionic strength dependence of the persistence length of some polyanions. The persistence length will be determined from the viscometric data analyzed by a fitting procedure with the aid of Fujii–Yamakawa relationship. A special emphasis will be placed on its comparison with the electrostatic persistence length theoretically calculated according to Odijk and Le Bret.

Experimental Section

Viscometric relationships $[\eta] = KM^{\nu}$ have been collected from the literature and presented in Tables I and II together with the range of molecular weight in which they are valid. The molecular weight M_0 and the length h of the monomer units are also given. When unspecified, the viscosity values refer to experiments performed in NaCl at 25 °C.

The Fujii–Yamakawa relationship for wormlike chains can be expressed as

$$[\eta] = \frac{\Phi_\infty M^{1/2}}{(M_L/2q)^{3/2}}\left[1 - \sum_{i=1}^{4} C_i\left(\frac{L}{2q}\right)^{-i/2}\right]^{-1} \quad \text{for } L/2q > 2.28 \quad (1)$$

if the intrinsic viscosity is expressed in cm^3·g^{-1}. Φ_∞ is the theoretical Flory constant for infinitely large molecular weights ($\Phi_\infty = 2.87 \times 10^{23}$) and M_L the mass per unit length, equal to the ratio M_0/h of the molecular weight to the length of the monomer unit. L represents the theoretical contour length or the degree of polymerization multiplied by h ($L = Mh/M_0$). C_i are coefficients that depend on the ratio $d/2q$, where d is the cylinder diameter according to expressions given in ref 10 for different $d/2q$ ranges.

The form of the Fujii–Yamakawa relationship is changed when the ratio $L/2q$, which defines the number of Kuhn statistical segments, is smaller than 2.28.

Our computation procedure associates the Fujii–Yamakawa relationship with a multiparametric nonlinear least-squares fitting program[23] which we have already used for fitting the field strength dependences of the electric birefringence of polyelectrolytes.[24] The parameters d and q were kept as variables, and the $[\eta]$ and M values are experimental ones when directly available from the literature or, when not available, a series of eight to ten $[\eta]$ and M values calculated from the viscometric relationships. This computation procedure is quite similar to that applied by Dayan et al.[12] in their study of the rigidity of cellulose derivatives. It is noteworthy that the two procedures have been tested with the

Table II
Experimental Molecular Weight–Viscosity Relationships, Persistence Length, and Diameter Obtained by the Procedure of Yamakawa and Fujii for Sodium Poly[((acrylamido)methyl)propanesulfonate] and Sodium (Carboxymethyl)cellulose

		lit. values			calcd values		
polyelectrolyte (ref)	I, mol·L^{-1}	$K \times 10^5$, dL·g^{-1}	ν	M range, M_0, and h	q, Å	d, Å	$Y \times 10^3$
sodium poly[((acrylamido)methyl)-propanesulfonate] (22)	0.01	0.83	1.0	$M = 1.4 \times 10^5$ to 9×10^5, $M_0 = 229$, $h = 2.5$ Å	170	1.5	1.4
	0.05	1.09	0.93		102	(0.5)	0.7
	0.1	1.64	0.88		77	1.7	0.6
	0.5	1.95	0.83		51	(0.5)	0.3
	1.0	3.60	0.77		40	1.2	0.2
	5.0	5.31	0.72		30	1.9	0.1
sodium (carboxymethyl)-cellulose[a] (21)	0.005	7.2	0.95	$M = 1.4 \times 10^5$ to 1.1×10^6, $M_0 = 247$, $h = 5.15$ Å	231	2.3	1.4
	0.01	8.1	0.92		184	(0.9)	1.1
	0.05	19.0	0.82		110	1.9	0.6
	0.2	43.0	0.74		80	4.9	0.4

[a] DS = 1.06.

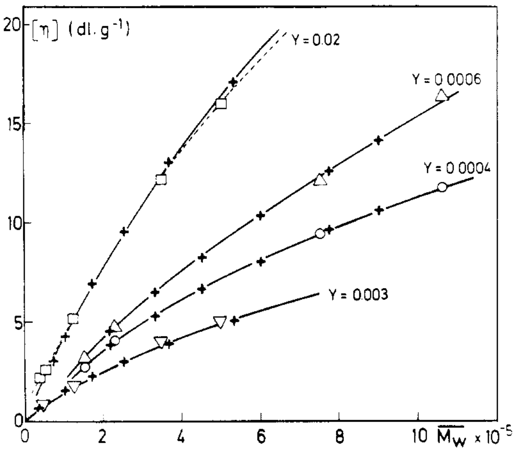

Figure 1. Some examples of fitting [η] vs. M experimental curves for PAANa in 0.01 (□) and 0.1 M (▽) NaBr and for CMCNa in 0.05 (△) and 0.2 M (○) NaCl.

same [η] and M values for poly(p-phenyleneterephthalamide) in sulfuric acid.[11] Dayan et al. found q and d values equal to 116 and 9 Å, whereas we obtained q = 114 Å and d = 9.7 Å. We also checked successfully our computation procedure with the [η] and M values determined for some other uncharged stiff polymers: poly(n-hexyl isocyanate)[25] and poly(phthaloyl-*trans*-2,3-dimethylpiperazine),[26] for which q values of respectively 350 and 27 Å have been obtained. For the latter polymer, a value of q = 33 Å was found by Motowoka et al.[26] Therefore, our computation method can be regarded with confidence, whatever the magnitude of the persistence length.

The quality of the fitting and hence the accuracy of the parameters issued therefrom are characterized by a parameter Y equal to the sum of the squares of the relative deviations:

$$Y = \sum_i (Y_{i,\text{measd}} - Y_{i,\text{calcd}})^2 / (Y_{i,\text{measd}} Y_{i,\text{calcd}}) \qquad (2)$$

This parameter can be used to define the "quality" of the fittings when the number of points are of the same order of magnitude. Good fittings are generally performed when Y is lower than 10^{-2}; some examples of fittings of [η] vs. M curves for PAANa and CMCNa are presented in Figure 1. A good accuracy can thus be expected for the persistence length value. The uncertainty in the diameter is much larger. Indeed, we observed during the fittings that a small change of q causes a nonnegligible change of d.

Results and Discussion

(1) Ionic Strength Dependence of the Measured Persistence Length. Tables I and II yield the q and d values, together with the Y parameter for PAANa, PAMPSNa, CMCNa, and sodium poly(styrenesulfonate) (PSSNa) in similar ionic strength ranges. For PAANa, we made use of the data of Takahashi[19] (I = 0.01–0.0025 M) and of Noda et al.[18] (I = 0.5–0.01 M). The latter data have been already analyzed by Kitano et al.,[13] who obtained q values slightly smaller than those given in Table I. For PAMPSNa, Fisher et al.[14] reported q values for one low and one high molecular weight fraction. We systematically reanalyzed the viscosity–molecular weight relationships with our procedure and obtained q values (Table II) in fairly good agreement with those reported in ref 14. They also agree with the q values derived from light scattering data.[14]

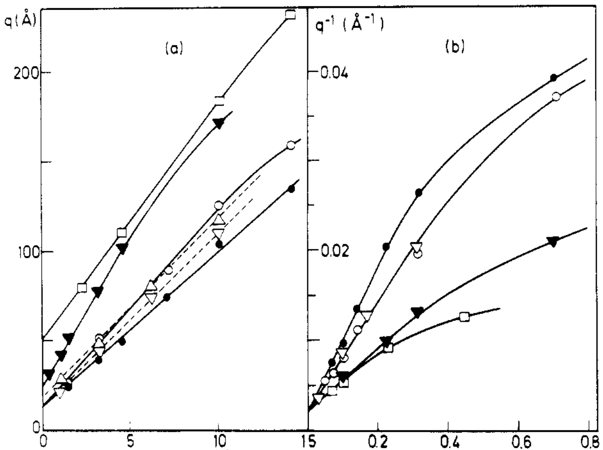

Figure 2. (a) Variations of the experimental persistence length with the reciprocal of the square root of the ionic strength for PAMPSNa (▼), CMCNa (□), PAANa (○), PSSNa (●), and PBVMANa at α = 0.5 (△) and α = 1.0 (▽). (b) Extrapolations of the reciprocal of the experimental persistence length to zero ionic strength.

For all the polyelectrolytes investigated, it is found that q displays the so-called "polyelectrolytic effect", i.e., a sharp increase with decreasing I. We also observed that the three vinylic polyelectrolytes, having different lateral groups bearing charged sites, differ in their persistence length. In Figure 2a, q is plotted against the inverse of the square root of the ionic strength and can be linearly extrapolated to $I^{-1/2} = 0$ (infinite ionic strength). The results of Miyamoto[15] for the PBVMANa at two degrees of neutralization (α = 1.0 and α = 0.5) are also presented. Such an extrapolation yields the persistence length of the polymer under conditions where the rigidity arises solely from the chain backbone and the steric hindrance effects of the lateral groups. These values of the persistence length l_p are of the same order of magnitude for all the vinylic polyions (14 Å for PAANa, PSSNa, and PVBMANa (α = 1.0), 18 Å for PVBMANa (α = 0.5), and 24 Å for PAMPSNa) but are larger for CMCNa (50 Å). It appeared interesting to compare l_p with the persistence lengths of uncharged polymers chosen as polymer models. Dayan et al. found for cellulose triacetate[12] q values ranging from 35 to 66 Å, depending on the nature of the solvent. Using the viscometric results of Moore and Brown[27] for ethylcellulose (containing 48.5% ethoxyethyl groups), we found q = 68 Å and d = 5 Å in benzene and in butanone. Moreover, Miyamoto determined the persistence length of an alternating copolymer (isobutyl vinyl ether–maleic anhydride) in the absence of counterions and found q = 12 Å, which is close to the extrapolated values (Figure 2a) of 18 and 14 Å at neutralization degrees of 0.5 and 1.0, respectively.

Making use of the data of Vink[17] for CMCNa and of Kay and Treloar[28] for PAANa, we analyzed the conformational behavior of these polyelectrolytes at very low ionic strength and in pure water. The fitting of the intrinsic viscosity values of PAANa (molecular weight range 1.5×10^4 to 5.0×10^4) in pure water yielded unrealistic values larger than 1200 Å for the persistence length, and a diameter of about 80 Å. Similar results were obtained for CMCNa (degree of substitution (DS) = 1.15) in 2×10^{-4} M NaCl: a persistence length of the order of 850 Å and a diameter larger than 100 Å. As previously reported, those peculiar values of the conformational parameters possibly arise from the electroviscous effect.

Figure 2b shows the variation of the reciprocal of the persistence length against ionic strength. The curves observed seem to tend toward a single q value of the order of 500 Å at zero ionic strength, at least for the vinylic polyions. Although this value is only a rough estimate, it should correspond to maximum rigidity in the absence of added salt. Such a result can be compared to the persistence length derived from the electrooptical results in pure water analyzed by means of the Stockmayer–Hearst relationships,[29,30] namely around 400 Å for poly(*N*-butyl-4-vinylpyridinium bromide), 200–250 Å for partially charged poly(*N*-methyl-2-vinylpyridinium bromide),[31] and around 300 Å for PSSNa.[32] Since the Stockmayer–Hearst theory has been criticized, it will be useful to analyze those data in terms of the new treatment recently developed by Yamakawa and Yoshizaki[33] for the rotational diffusion coefficient of wormlike and helical wormlike chains. Presently, we can only conclude that the persistence length of polyions that possess a rather flexible backbone reaches, as a consequence of the effect of electrostatic repulsion, a value close to that of polymers with a very rigid backbone: around 395–425 Å for poly(*n*-hexyl isocyanate).[34]

Some caution should be exercised when these experimental values of the persistence length are compared with theoretical ones because the former remain subject to two major uncertainties. First, recent rigorous measurements of translational diffusion showed that the friction coefficients of certain polyelectrolytes reach values markedly smaller than those expected for an ideal wormlike coil of similar persistence length. In that sense, additional friction phenomena occur when isolated polyions translate through low ionic strength media and thus should markedly influence the intrinsic viscosity.[35,36] Secondly, it should be emphasized that the experimental persistence length values derived from viscosity data in good solvents are affected by the excluded volume effect. In fact, expansion of the polyion arises from electrostatic short-range interactions, involved in the persistence segment, and from electrostatic and nonelectrostatic long-range interactions between noncontiguous segments, involved in the excluded volume. Attempts have been made to evaluate this influence on the persistence length of wormlike chains, namely by Manning in the case of light scattering data on DNA[37] and by Kamide and Saito in the case of viscosity data on cellulose derivatives.[38] In his study of the rigidity of PVBMANa, Miyamoto considered that the excluded volume effect may be neglected in first approximation in the ionic strength range 0.01–1.0 M. Both effects, added translational friction and excluded volume, are expected to increase with decreasing ionic strength, so that the persistence length values collected in the present study should be considered as upper limits, as noticed by Schurr and Allison.[36] A nonnegligible discrepancy between the measured and the effective persistence length should exist in media of low ionic strength (0.01 M and below).

(2) Calculation of the Electrostatic Persistence Length. Odijk[1-4] and Skolnick and Fixman[5] derived simultaneously and independently, on the basis of a linearized form of the Poisson–Boltzmann equation, an expression relating l_e to the total ionic strength:

$$l_e = Q/4\kappa^2 b^2 \qquad (3)$$

where $Q = e^2/4\pi\epsilon_0\epsilon kT$ is the Bjerrum length, e the elementary electric charge, ϵ_0 the permittivity of a vacuum (8.85×10^{-12} F·m^{-1}), ϵ the dielectric constant of the medium, and kT the Boltzmann energy factor. b represents the distance between charged sites and κ^{-1} the Debye–Hückel screening length, directly related to the ionic strength I (in mol·L^{-1}) through the relationship

$$\kappa^2 = 8\pi \times 10^3 N_{\text{Avogadro}} Q I \qquad \text{(SI units)} \qquad (4)$$

Q is equal to 7.135 Å for water at 25 °C.

Provided that $Q \geq b$, eq 3 is reduced to

$$l_e = 1/4\kappa^2 Q \qquad (5)$$

and it is expected that the latter equation holds as long as the so-called "local stiffness approximation" $(l_e + l_p) \gg 1$ is verified.[4,5]

Recently, Fixman[6] and Le Bret[8] reported new treatments for estimating the electrostatic contribution to the persistence length. Le Bret has integrated numerically the complete Poisson–Boltzmann equation for a toroid. Its results cannot be put into analytical relationships and are collected in ref 8 as tables giving l_e as a function of the ionic radius a, the Debye–Hückel parameter κ, and the linear density charge $\lambda = Q/b$. In the particular case of DNA (a = 10 Å, λ = 4.2), the calculated l_e values are close to the experimental persistence lengths determined by Borochov et al.[39] in the high ionic strength range from light scattering data and by Hagerman[40] in the low ionic strength range from the relaxation time of the electric birefringence. It is worth noting the two experimental procedures yield consistent q values at comparable ionic strength, namely 530 and 500 Å at I = 0.005 M. Otherwise, the theoretical l_e values for DNA issued from the treatments of Le Bret and Fixman are practically the same. If we except the very low ionic strength medium (10^{-4} M), not considered in the present paper, the difference between the l_e values given by the two treatments is negligible.[6]

Experimental values of $l_e = q - l_p$ from Tables I and II show (Figure 3) linear dependence on the reciprocal of the square root of the ionic strength in the 0.01–1.0 M range. Such linear variations previously detected for PAANa[13] and PBVMANa[15] seem to be common for a wide variety of polyelectrolytes. They however markedly depart from the I^{-1} dependence predicted in the initial theories of Odijk[4] and Skolnick and Fixman.[5] In addition, the l_e values calculated according to eq 5 are smaller than the experimental ones (Figure 3). A possible origin of this discrepancy could be related to the local stiffness ap-

Table III
Theoretical Values of the Electrostatic Persistence Length at Various Ionic Strengths according to the Treatments of Odijk, Skolnick, and Fixman and of Le Bret

theory of Odijk, Skolnick, and Fixman				theory of Le Bret					
				$\lambda = 3$, $a = 8$ Å (PSSNa and PAMPSNa)		$\lambda = 3$, $a = 3$ Å (PAANa)		$\lambda = 1.5$, $a = 8$ Å (CMCNa)	
I, mol·L^{-1}	$\kappa \times 10^{-8}$, m^{-1}	l_e, Å	κa	I, mol·L^{-1}	l_e, Å	I, mol·L^{-1}	l_e, Å	I, mol·L^{-1}	l_e, Å
0.001	1.047	320	0.0336	0.00016	1702	0.00114	240	0.00016	1424
0.002	1.481	160	0.0625	0.00056	615	0.00396	86	0.00056	493
0.005	2.342	64	0.1061	0.0016	287	0.0114	40	0.0016	218
0.01	3.322	32	0.3357	0.016	90	0.114	13	0.016	54
0.02	4.684	16	1.0615	0.163	45	1.141	6.4	0.163	19
0.05	7.406	6.4	3.3568	1.631	22	11.41	3.1	1.631	6.3
0.1	10.47	3.2							
0.2	14.81	1.6							
0.5	23.42	0.64							

Table IV
Persistence Length and Diameter Values of PAANa at Various Ionic Strengths as a Function of the Degree of Neutralization

	$\alpha = 0.103$		$\alpha = 0.2$		$\alpha = 0.4$		$\alpha = 0.6$	
I	q, Å	d, Å	q, Å	d, Å	q, Å	d, Å	q, Å	d, Å
0.5	11	4.9	16	4.9	23	3.0	30	3.7
0.1	24	1.9	39.0	2.8	39	1.0	59	2.2
0.025	45	(0.7)	75	1.1	95	(0.7)	116	1.9
0.01	70	(0.1)	122	(0.8)			151	3.4
	$\lambda = 0.299$		$\lambda = 0.571$		$\lambda = 1.142$		$\lambda = 1.71$	
	$h = 1.6$ Å		$h = 1.6$ Å		$h = 2$ Å		$h = 2$ Å	
	$M_0 = 74.3$		$M_0 = 76.4$		$M_0 = 80.8$		$M_0 = 85.2$	

proximation mentioned above. As an example, the product $\kappa(l_e + l_p)$ or κq for PSSNa, calculated from the data of Tables I and III, is of the order of 3–4 in the 5×10^{-3} to 10^{-1} M ionic strength range. Since, this product cannot be considered as being much larger than unity, the validity of the local stiffness approximation could be questioned under these conditions.

The electrostatic persistence lengths calculated according to Le Bret are given in Table III. For all the fully charged vinylic polyelectrolytes, the linear density charge is constant and equal to 2.85 (b = 2.5 Å). For CMCNa, with a monomer length of 5.15 Å and a degree of substitution of 1.06, λ is smaller and equal to 1.47. The ionic radius a is the distance separating the charged sites from the axis of the polyion and is estimated from the bond lengths and valence angles as a = 3 Å for PAANa and a = 8 Å for PSSNa, PAMPSNa, and CMCNa. For the latter polyelectrolytes, a radius of 8 Å was calculated by assuming that the carboxymethylation mainly affects the CH_2OH groups of cellulose. Tables 1 and 2 of ref 8 give l_e (calculated for a radius of 10 Å) as a function of λ for different values of the κa product. It is thus possible to determine l_e for other values of the radius since we have[8]

$$\kappa_1 a_1 = \kappa_2 a_2 \quad (6)$$

$$l_e(\kappa_2 a_2) = (a_2/a_1)^2 l_e(\kappa_1 a_1) \quad (7)$$

The variations of $l_{e,\text{theor}}$ as a function of ionic strength have been established for two values of the linear density charge, 1.5 and 3.0, which are close to those of our polyelectrolytes. It appears immediately that $l_{e,\text{theor}}$ does not vary linearly with $I^{-1/2}$ as observed for $l_{e,\text{exptl}}$. Nevertheless, a reasonable agreement is observed for PAMPSNa and PSSNa: for the former, the $l_{e,\text{theor}}$ values agree with the experimental ones at high ionic strength and a discrepancy by a factor of about 1.4 is noticed at $I \sim 0.01$ M. For the latter, the $l_{e,\text{theor}}$ values are approximately 1.2–1.5 times larger than the experimental ones over the whole ionic strength range. The discrepancy is more important for CMCNa and PAANa ($l_{e,\text{exptl}}/l_{e,\text{theor}}$ = 1.7–2.0). As recently suggested by Hagerman,[41] the electrostatic "end effects" may markedly affect the l_e values, particularly in the case of short chains.

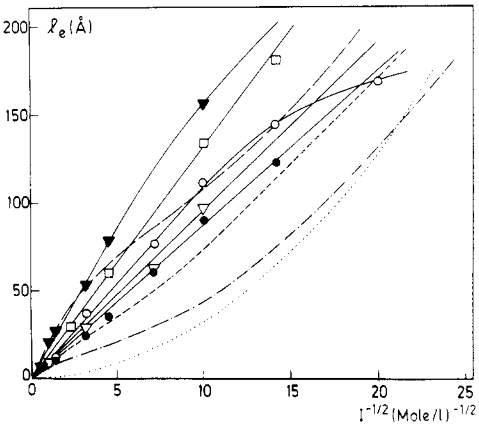

Figure 3. Ionic strength dependence of the experimental persistence length of PAMPSNa (▼), CMCNa (□), PAANa (○), PSSNa (●), and PBVMANa at α = 1.0 (▽); comparison with values calculated according to the procedure of Odijk, Skolnick, and Fixman (···) and of Le Bret: PAMPSNa and PSSNa (– – –), CMCNa (---), and PAANa (–··–).

(3) Influence of the Degree of Ionization on the Persistence Length. Noda et al. have established the viscosity–molecular weight relationships for PAANa at various degrees of ionization α. From the coefficients of the Kuhn–Mark–Houwink relationships collected in Table II from ref 18, it is possible to estimate the persistence length values as a function of the linear density charge, expressed here as $\lambda = Q\alpha/b$. The results of the fittings are presented in Table IV. For the lower degrees of ionization α = 0.1 and 0.2, good fittings can only be obtained by taking an effective h value of 1.6 Å, which is smaller than the monomer length unit. For α = 0.4 and α = 0.6, we took h = 2 Å. All fittings made with h = 2.5 Å yield

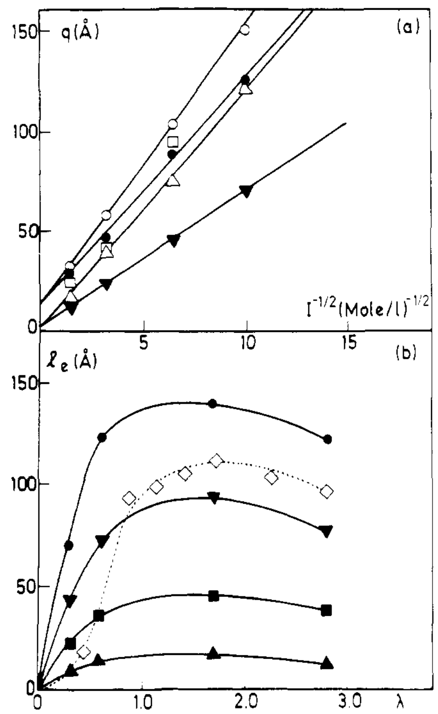

Figure 4. (a) Variations in the experimental persistence length with the reciprocal of the square root of the ionic strength for PAANa at various degrees of neutralization. (b) Variations in the experimental electrostatic persistence length for PBVMANa at I = 0.01 M (◊) and for PAANa at four ionic strengths: 0.5 (▲), 0.1 (■), 0.025 (▼), and 0.01 M (●).

unrealistic values of the diameter, generally lower than 0.1 Å. Figure 4a shows that the previously determined linear $I^{-1/2}$ dependence of the persistence length is verified, whatever the degree of ionization. The l_p values at infinite ionic strength are equal to 2 Å for α = 0.1 and 0.2 and 14 Å for α = 0.6 and 1.0. In Figure 4b, the l_e values are plotted as a function of λ for different ionic strengths. All curves seem to pass through maximum values around λ ~1.1–1.5 ($\alpha \sim$ 0.4–0.5) and then very slightly decrease for higher λ values. Such an effect can be tentatively explained on the basis of the counterion condensation. Working here with polyelectrolytes at infinite dilution, we can accept the model of Manning and consider that the apparent charge parameter is equal to λ for λ values smaller than unity in the case of monovalent counterions. For $\lambda \geqslant 1$, this parameter is then equal to unity. The counterion condensation takes place and keeps constant the apparent charge of the polyion.[42,43] The increase of l_e thus reflects the progressive increase of the apparent charge parameter and of the involved repulsion between charged sites. In that case, the slight decrease recorded for large λ values should be regarded as having minor significance. A quite similar behavior has been detected with the data of Miyamoto for PBVMANa at I = 0.01 M (Figure 4b). The comparison between experimental and theoretical l_e values for PAANa as a function of degree of ionization has also been investigated, but unfortunately it yields no significant results. For instance, the discrepancy $l_{e,\mathrm{exptl}}/l_{e,\mathrm{theor}}$ at I = 0.01 M is of order of 2.5–4, depending on the range of the linear density charge. It has been seen in the preceding section that, among the various fully charged polyelectrolytes studied, PAANa shows the largest discrepancy between experimental and theoretical l_e values.

Conclusions

The measured persistence length very precisely reflects the conformational changes of polyelectrolytes with concentration of added salt. It is observed that the persistence lengths of four different vinylic polyelectrolytes approach similar values at zero ionic strength, roughly estimated to be 500 Å. In addition, evaluation of persistence length values at infinite ionic strength l_p showed a very good agreement with that of uncharged polymers of similar structure. The rigidity of the fully coiled polyions solely depends in this case on the chain skeleton and on the nature of the side groups. Such a procedure involving extrapolations of the persistence length to zero and infinite ionic strength gives access to the variation of the persistence length over the whole ionic strength range. It however requires that the viscosity–molecular weight relationships are known in the 1.0–0.005 M ionic strength range.

The electrostatic contribution to the persistence length $l_e = q - l_p$ appeared to vary linearly with $I^{-1/2}$ and to depend upon the nature of the charged side groups, contrary to the earlier Odijk–Skolnick–Fixman theory, which predicts an I^{-1} dependence that is similar for all polyelectrolytes. Better agreement can be found with the theoretical l_e values calculated with the aid of more recent theories of Le Bret[8] and Fixman.[6] The variation of $l_{e,\mathrm{theor}}$ vs. $I^{-1/2}$ is more closely approached. A semiquantitative agreement was obtained for the PSSNa and PAMPSNa samples where the discrepancy factor did not exceed 1.2–1.5. The influence of the lateral group was taken into account in the distance separating the ionic site from the main axis of the polyion. Furthermore, the present study indicates there is a possibility for investigating the influence of several factors related to the nature of the polymer or of the medium on the persistence length of polyelectrolytes. A hydrodynamic parameter such as the intrinsic viscosity or the sedimentation, translational, or rotational diffusion coefficient should be measured as a function of the molecular weight and analyzed in terms of the Yamakawa theory.

The origin of the discrepancy between calculated and experimental persistence lengths should arise not only from the theory but also from a large uncertainty due to the additional friction and excluded volume effects affecting the experimental values. Both are expected to increase with decreasing concentration of added salt and cause an overestimation of the persistence length values.

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Registry No. PAANa, 9003-04-7; PSSNa, 9080-79-9; PAMPSNa, 55141-01-0; CMCNa, 9004-32-4; PBVMANa, 77017-85-7.

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Simple Model for Clustering and Ionic Transport in Ionomer Membranes

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ABSTRACT: Cluster formation of the ionic side groups in an ionomer membrane of the Nafion type has been modeled and its relationship to ionic transport examined. Computer simulations show that the effect of electrostatic and elastic forces on the pendant ionic groups and their neutralizing counterions is such as to form a dipole layer at the surface of an ionic cluster. A model for selective transport is proposed based on the electrostatic potential created by the dipole layer. Qualitative agreement with experiment is obtained for the cluster size and current efficiency as a function of the equivalent weight of the membrane.

I. Introduction

Ion-containing polymer membranes exhibit a sizable difference in permeability between oppositely charged ionic species. Although the origin of this phenomenon is not well understood, it is generally believed that permselectivity arises as a consequence of the electrostatic interaction at the ion exchange sites in the membrane.[1] The ionic groups of the ionomer phase separate into clusters, forming a hydrophilic ionic phase in a hydrophobic polymer matrix.

In this paper we report the results of a modeling of cluster formation in an ionomer membrane and its relation to ionic transport through the membrane. In particular, we consider a system of the Nafion type and describe computer simulations of the spatial organization of ion dipoles within a cluster and have examined the relationship of this structure to ionic transport. The ionomer model that we have considered is highly simplified, containing only the most important ingredients in the problem, namely, the electrostatic and the elastic contributions to the energy. Our calculation is similar, in principle, to that of Eisenberg,[2] with the important difference that we do not assume any particular orientation for any dipole but rather treat these orientations as parameters that must be allowed to vary as the system minimizes its free energy and seeks its most favorable configuration. Perhaps the most interesting result to emerge from our simulations is that under the influence of electrostatic forces alone the ionic dipoles orient themselves to lie in the surface of the spherical clusters. There is thus no effective dipole layer at the cluster surface and the boundary is symmetric to the flow of cations and anions. However, as one will see in section III, the process of cluster formation gives rise to an elastic energy that breaks this symmetry and leads to selective transport.

II. Definition of the Model

While it is clear from experimental observation that clustering of the pendant-side-chain ionic groups does occur, the precise form of these clusters has not been determined. Some evidence exists[3] to suggest that the clusters may deviate from spherical form, possibly even being tubular in nature. In the present work we will make the simpler assumption that the dipolar ionic groups are distributed over the surface of a spherical cluster. We will thus base our calculations on a geometry very similar to that of the inverted-micelle model proposed by Gierke.[4] In choosing this model we are not denying the possibility that the dipoles may form a volume distribution within the cluster; we are rather taking as our first model the more plausible case in which the surface distribution of dipoles is not penetrated by segments of inert chain backbone, with the attendant energy cost. We further assume that the ionic groups, which are taken to be neutralized by counterions and exist in the form of ion pairs or dipoles, form a close-packed arrangement on the surface of the cluster, the nearest-neighbor distance being determined by the molecular pair potential. As mentioned in the Introduction, we consider only elastic and electrostatic effects. The driving force for clustering results from the fact that the electrostatic energy is lowered when dipoles

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