Studies of Polyelectrolyte Solutions III. Correlations between the Second and the Third Virial Coefficient

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ABSTRACT: Combined Donnan equilibria and static light scattering experiments have been performed on aqueous solutions of poly(styrene sulfonate), PSS, in the presence of low molar mass electrolytes. Two systems were investigated, namely PSS/Na and PSS/Pb/H. The coion was nitrate. Additionally, the molar mass, M_w , of PSS was varied in the range of 3.20×10^5 to 1.22×10^6 Da. Donnan equilibria experiments yield the degrees of binding, Θ_1 and Θ_2 , for the uni- and the divalent counterions. Θ_1 and Θ_2 increase with increasing ionic strength, but they are independent on M_w within the experimental error. Static light scattering yields the molar mass, M_w , the radius of gyration, $\langle S^2 \rangle_z^{1/2}$, and the second and third virial coefficients, A_2 and A_3 . Data analysis is made in two ways: (1) by using the brute-, and (2) by using the net polyion concentrations. Here, the term "brute" stands for the naked polyion skeleton, while the net polyion concentration is the concentration which includes the counterions bound to the polyelectrolytes. C_{brute} is known from the sample preparation. C_{net} can be calculated from Θ_1 and Θ_2 . It is found: (1) $M_{w,\text{net}}$ is significantly larger than $M_{w,\text{brute}}$; (2) $\langle S^2 \rangle_{z,\text{net}}^{1/2}$ and $\langle S^2 \rangle_{z,\text{brute}}^{1/2}$ are identical within the experimental error, and (3) $A_{2,\text{net}}$ and $A_{3,\text{net}}$ are significantly smaller than $A_{2,\text{brute}}$ and $A_{3,\text{brute}}$. The molar mass dependencies of $\langle S^2 \rangle_{z,\text{net}}^{1/2}$, $A_{2,\text{net}}$, and $A_{3,\text{net}}$ can be well described by power laws $\langle S^2 \rangle_{z,\text{net}}^{1/2} = K_{\langle S \rangle_z} \cdot M_{w,\text{net}}^{v_{\langle S \rangle_z}}$, $A_{2,\text{net}} = K_{A_2} \cdot M_{w,\text{net}}^{v_{A_2}}$, and $A_{3,\text{net}} = K_{A_3} \cdot M_{w,\text{net}}^{v_{A_3}}$. The exponents, $v_{\langle S \rangle_z}$ and v_{A_3} , decrease with increasing ionic strength while $|v_{A_2}|$ increases. Interestingly, v_{A_3} is significantly larger than $2v_{A_2} + 1$. This suggests that A_3 is not proportional to $A_2^2 \cdot M_w$ as predicted by some theories. The nature of the mentioned effects could be established, however, only in part. An interpretation by the conventionally excluded volume theory was not successful. Indeed, a universal function, Ψ , incorporating effects such as molar mass, degree of dissociation, and solvent quality, is found; but none of the present theories is suitable to describe the experimental data satisfactory. In conclusion, a completely new theoretical concept will be necessary for the future.

KEY WORDS Poly(styrene sulfonate) / Static Light Scattering / Counterion Condensation / Brute and Net Quantities / Second and Third Virial Coefficient / Excluded Volume /

Physical properties of poly(styrene sulfonate), PSS, in dilute aqueous solutions containing low molar mass electrolytes in excess have been studied previously^{1,2} *via*. Donnan dialysis equilibrium, viscosity, and static light scattering. The results obtained for the systems PSS/Pb/H, PSS/Pb/Na, and PSS/Na have shown that (1) the degrees of counterion condensation are well predicted by the two-variable theory of Manning³; that (2) a PSS-ion behaves like an extended worm-like coil; and

that (3) the magnitude of the radius of gyration is predominantly influenced by the number of totally nonneutralized charges per PSS-ion.

In the present work, we continue our previous study. The purpose is threefold. First, the influence of the molar mass, M_w , on the degree of binding, Θ_1 , for the univalent counterion Na is studied. This is of interest because according to Manning³ there should be no dependence of Θ_1 on M_w . Second, the molar mass dependencies of the radius of gyration,

$\langle S^2 \rangle_z^{1/2}$, and those of the second and third virial coefficients, A_2 and A_3 , are examined in the range of accessible ionic strengths, I . Different behavior can be expected because $\langle S^2 \rangle_z^{1/2}$ is a geometrical quantity, while A_2 and A_3 are thermodynamic ones. Third, we try to interpret the interrelations found between $\langle S^2 \rangle_z^{1/2}$, A_2 , and A_3 . This is made by proving the present intra- and intermolecular excluded volume theories,⁴⁻⁶ including the expansion factor, α , and the interpenetration function, Ψ . Special attention is paid to the interrelation between A_2 and A_3 which is discussed within the lattice-theory of Post and Zimm⁷.

The data analysis itself is made in two different ways. First, the light scattering data are analyzed by using the brute polyion concentration, C_{brute} . This is related to the model that all counterions surrounding a polyion are free, but building a Debye-Hückel atmosphere. C_{brute} is thus identical with the concentration of the naked polyion scaffold.

The above idea governed the polyelectrolyte research up to 1970. With the springing up of Mannings studies⁸⁻¹⁰ it became, however, more and more clear that a certain part of the counterions is directly bound or condensed to a polyion. The actual molar mass of a polyion is thus significantly larger than that of the skeleton and it is necessary to introduce a net polyion concentration, C_{net} . This is given as the sum of C_{brute} and the concentration of the counterions totally bound to the polyions, both in g per liter. Note, C_{brute} is known from the sample preparation and C_{net} can be calculated exactly from C_{brute} and Θ_1 and Θ_2 .

As a consequence, two data sets are obtained for M_w , $\langle S^2 \rangle_z^{1/2}$, A_2 , and A_3 , one for C_{brute} and one for C_{net} . Quantitatively different behavior is, however, expected only for M_w , A_2 , and A_3 . This is because M_w , and A_2 and A_3 are quantities given by the concentration dependence of the scattered light intensity, I_{sc} , while $\langle S^2 \rangle_z^{1/2}$ is obtained from the angular dependence of I_{sc} . To prove this, the system

PSS/Pb/H may be the most suitable one. This is because the molar mass of Pb is about a factor of 9 larger than that of Na. Thus, the effect of counterion condensation on C_{net} should be more profound for Pb^{2+} than for Na^+ -ions.

EXPERIMENTAL

Materials

Sodium poly(styrene sulfonate), NaPSS, was purchased from Pressure Chemical Co., Pittsburgh. The samples were prepared by sulfonation of well-defined monodisperse polystyrene. Purification and conversion to the H-form was made by dialysis as described by Kwak.¹¹ After that the molar masses, M_w , were determined by small angle light scattering in 1 N HNO_3 at $T=20^\circ\text{C}$. Three samples were used and $M_{w,\text{brute}}$ was found to be 3.20×10^5 , 7.28×10^5 , and $1.22 \times 10^6 \text{ g mol}^{-1}$. Elemental analysis shows that the degree of sulfonation is 84% for $M_w=3.20 \times 10^5 \text{ g mol}^{-1}$ and nearly 95% for the two other M_w . This gives charge density parameters of $\xi=2.40$ and 2.74, respectively.

Solutions were prepared with filtered, deionized, and double distilled water. They were freed from dust by filtering through $0.22 \mu\text{m}$ filters and dialyzed exhaustively against dust-free electrolyte solution of known ionic strength in a special cell. After reaching the Donnan equilibrium the samples were filled directly into the light scattering cells. The final PSS-concentrations were determined spectrophotometrically at 261 nm by using a Hitachi spectrometer.

Static Light Scattering Measurements

The instrument used was an ALV-3000 spectrometer.¹² The scattered intensities, I_{sc} , were recorded at 20°C using unpolarized light of 632.8 nm. This was emitted from a He-Ne laser (Spectra-Physics). Measurements were performed over the angular range of 20 to 140° . The intensities, I_{sc} , were first corrected for the

scattering from pure solvent, and subsequently analyzed by using the generalized Zimm-equation.¹³ For further details we refer to the previous paper.²

RESULTS AND DISCUSSION

Donnan Dialysis Equilibrium and Light Scattering

The brute molar mass, $M_{w,brute}$, of a PSS-ion is given by:

$$M_{w,brute} = \langle P \rangle [(1 - \delta)M_{St} + \delta M_{SS-}] \quad (1)$$

$\langle P \rangle$ is the average degree of polymerisation of a PSS-polyion and δ is its degree of sulfonation. M_{St} and M_{SS-} are the molar masses of styrene and ionized styrenesulfonate. For the PSS-samples studied here, we find the values $M_{w,brute} = 3.20 \times 10^5$, 7.28×10^5 , and 1.22×10^6 g mol⁻¹.

The net molar mass, $M_{w,net}$, of a PSS-polyion to which both uni- and divalent counterions are condensed or bound is, on the other hand, given by

$$M_{w,net} = \langle P \rangle [(1 - \delta)M_{St} + \delta(M_{SS-} + \Theta_1 M_1 + \Theta_2 M_2)] \quad (2)$$

Here, Θ_1 and Θ_2 are the degrees of uni- and

divalent counterion condensation. M_1 and M_2 are the counterion molar masses.

Values of Θ_1 and Θ_2 are obtained by the method of Donnan dialysis equilibrium. See, for instance, ref 1. That is, all parameters of eq 2 are known and $M_{w,net}$ can be determined without difficulty.

To indicate the method used for the evaluation of $M_{w,net}$, we add the suffixes "D" or "LS" to $M_{w,net}$. "D" stands for dialysis equilibrium. That is $^D M_{w,net} = M_{w,net}$, where $M_{w,net}$ is given by eq 2. "LS" in $^{LS} M_{w,net}$ stands for light scattering.

Typical results are collected in Table I. They refer to the systems PSS/Pb/H and PSS/Na.

Note, the $^{LS} M_{w,net}$ -values were determined by inserting C_{net} into the generalized Zimm-equation. C_{net} is thus given by $C_{net} = ^D M_{w,net} \cdot C_p$ with C_p being the molar number of PSS-molecules per liter. That is, theoretically $^D M_{w,net}$ and $^{LS} M_{w,net}$ should be identical. Light scattering measurements are, however, affected by experimental errors between 5 and 10% in M_w . This leads to the deviations observed in Table I.

Table I shows also that the effect of counterion condensation on $^{LS} M_{w,net}$ is only profound if the molar mass of the counterions

Table I. Degrees of counterion condensation and polyion masses

PSS/Pb/H				PSS/Na		
Θ_1^a	Θ_2^b	$^D M_{w,net} \times 10^{-5}$	$^{LS} M_{w,net} \times 10^{-5}$	Θ_1^b	$^D M_{w,net} \times 10^{-5}$	$^{LS} M_{w,net} \times 10^{-5}$
		g mol ⁻¹	g mol ⁻¹		g mol ⁻¹	g mol ⁻¹
0.62	0.00	3.20	3.3	0.56	3.39	3.3
0.47	0.08	3.46	3.2	0.62	3.41	3.2
0.37	0.14	3.65	3.6	0.62	3.41	3.3
0.27	0.20	3.84	3.8	0.64	3.42	3.4
0.18	0.26	4.04	4.1	0.65	3.42	3.5
0.13	0.29	4.14	4.0	0.67	3.43	3.4
0.11	0.31	4.20	4.2	0.71	3.45	3.4
0.08	0.33	4.26	4.2	0.78	3.47	3.6
0.05	0.35	4.33	4.4	0.88	3.51	3.6
0.00	0.42	4.56	4.8			

^a Related to $C_p = 0$; $I = 0.01$ M and $T = 20^\circ\text{C}$.

^b See ref 2.

is large. The molar mass of Na is rather small compared to that of Pb. The changes found in $^{LS}M_{w,net}$ for the system PSS/Na are therefore within the experimental error, while a clear trend ($^{LS}M_{w,net} \sim \Theta_2$) is observed for the system PSS/Pb/H.

Next, we consider the brute and net-values of $\langle S^2 \rangle_z^{1/2}$, A_2 , and A_3 . They are obtained by inserting either C_{brute} or C_{net} into the generalized Zimm-equation. Note, also the refractive index increment must be calculated correctly. For instance, $dn/dC|_{\mu,net}$ is given by $\Delta n/C_{net}|_{\mu}$ where Δn is the difference in the refractive index between the PSS-solution and the appertaining solvent at the Donnan equilibrium. It should be also pointed out that the values of A_2 and A_3 depend sensitively on the procedure used for their calculation. Here, A_2 and A_3 were computed by the polynomial fit

$$\left. \frac{KC}{R} \right|_{q=0} = \frac{1}{M_w} + 2A_2C + 3A_3C^2 \quad (3)$$

with $C = C_{brute}$ or $C = C_{net}$, respectively. Note, q is the wavevector and KC/R refers to $q=0$. Some typical plots of $KC_{net}/R|_{q=0}$ vs. C_{net} are shown in Figure 1. It is seen that all curves are well described by eq 3. That is, the influence of A_3 cannot be neglected as is often done.

We should also note that for larger concentrations as those considered here, the

upward curvature of the KC/R vs. C -curves changes to a downward curvature. The polyions begin then to overlap with each other, so that the fourth virial coefficient, A_4 , becomes important. We are, however, interested only in the dilute region. For the behavior of polyelectrolytes in semidilute and concentrated solutions we refer to the studies of Mandel *et al.*¹⁴

Table II shows some typical results obtained for $\langle S^2 \rangle_z^{1/2}$, A_2 , and A_3 . The data refer to the system PSS/Pb/H. $M_{w,brute}$ is 3.20×10^5 Da. Qualitatively similar effects are observed,

Figure 1. Plots of $KC/R|_{q=0}$ vs. C_{net} . The system is PSS/Na and $M_{w,brute}$ is 7.28×10^5 Da. $I=0.005$ (1), 0.01 (2), 0.02 (3), 0.10 (4), and 1 M (5).

Table II. Brute and net quantities of the system PSS/Pb/H

$Z_{e,net}$	$\langle S \rangle_{z,net}^a$	$A_{2,brute} \times 10^3$	$A_{2,net} \times 10^3$	$A_{3,brute} \times 10^3$	$A_{3,net} \times 10^3$
	nm	cm ³ mol g ⁻²	cm ³ mol g ⁻²	cm ⁶ mol g ⁻³	cm ⁶ mol g ⁻³
597	44.0	2.53	2.53	74.8	74.8
580	42.0	1.54	1.48	33.3	32.6
550	39.8	0.92	0.85	27.2	25.8
518	35.5	0.44	0.39	10.2	9.4
471	33.0	0.22	0.19	7.0	5.8
456	32.0	0.18	0.15	6.6	5.2
424	30.5	0.13	0.10	6.2	4.8
408	30.0	0.089	0.056	6.2	4.6
393	29.5	0.052	0.027	6.0	4.5
252	27.5	0.006	0.003	5.9	4.4

^a $\langle S^2 \rangle_{z,brute}^{1/2} = \langle S^2 \rangle_{z,net}^{1/2}$, $T=20^\circ\text{C}$.

however, for all other systems. First, we see, there is only one value given for $\langle S^2 \rangle_z^{1/2}$. This is because the brute and the net values of the radius of gyration, $\langle S^2 \rangle_{z,\text{brute}}^{1/2}$ and $\langle S^2 \rangle_{z,\text{net}}^{1/2}$, are equal within the experimental error of 5 to 10%. Second, we see that the net-values of A_2 and A_3 are significantly smaller than the corresponding brute values. This is most marked for the system PSS/Pb/H, where the deviations between $A_{2,\text{brute}}$ and $A_{2,\text{net}}$ and $A_{3,\text{brute}}$ and $A_{3,\text{net}}$, respectively, increase as Θ_2 is raised. These differences become more and more unimportant with decreasing counterion molar mass until at the limit of ions such as H or Li they can be neglected at all.

The probable reason why the virial coefficients depend on the definition of the concentration, but the radii of gyration do not, is mainly due to the fact that the formers are parameters representing concentration dependencies, but the latter are not. That is, our observations are in line with our expectation. However, the true reason is not yet clear. The differences observed may be apparent.

Molar Mass Dependencies of $\langle S^2 \rangle_z^{1/2}$, $A_{2,\text{net}}$, and $A_{3,\text{net}}$

Tables III and IV contain the dialysis and light scattering results obtained for the three molar masses $M_{w,\text{brute}} = 3.28 \times 10^5$, 7.28×10^5 ,

Table III. Molecular characteristics of the system PSS/Na

I/M	$M_{w,\text{brute}} = 3.20 \times 10^5 \text{ Da}$			$M_{w,\text{brute}} = 7.28 \times 10^5 \text{ Da}$			$M_{w,\text{brute}} = 1.22 \times 10^6 \text{ Da}$		
	Θ_1	$\langle S \rangle_z^*$ ^a	α^b	Θ_1	$\langle S \rangle_z^*$	α	Θ_1	$\langle S \rangle_z^*$	α
0.005	0.56	48	1.76	0.62	77	2.03	0.64	110	2.20
0.01	0.62	45	1.65	0.64	72	1.89	0.64	103	2.06
0.02	0.62	43	1.58	0.66	68	1.79	0.68	95	1.90
0.05	0.64	41	1.51	0.68	63	1.66	0.69	86	1.72
0.10	0.65	38	1.40	0.68	58	1.53	0.70	78	1.56
0.20	0.67	36	1.32	0.70	54	1.42	0.71	73	1.46
0.50	0.71	33	1.21	0.73	48	1.26	0.74	64	1.28
1.00	0.78	30	1.10	0.80	43	1.13	0.78	57	1.14
2.00	0.88	28	1.03	0.88	40	1.05	0.86	53	1.06

^a $\langle S \rangle_z^* = \langle S^2 \rangle_z^{1/2} / \text{nm}$.

^b $\alpha = (\langle S^2 \rangle_z / \langle S^2 \rangle_{z,\Theta})^{0.5}$.

Table IV. Second and third virial coefficients of the system PSS/Na

I/M	$M_{w,\text{brute}} = 3.20 \times 10^5 \text{ Da}$		$M_{w,\text{brute}} = 7.28 \times 10^5 \text{ Da}$		$M_{w,\text{brute}} = 1.22 \times 10^6 \text{ Da}$	
	$A_{2,\text{net}}^*$ ^a	$A_{3,\text{net}}^*$ ^b	$A_{2,\text{net}}^*$	$A_{3,\text{net}}^*$	$A_{2,\text{net}}^*$	$A_{3,\text{net}}^*$
0.005	3.12	322	2.78	535	2.56	747
0.01	2.05	72.3	1.79	118	1.65	170
0.02	1.50	32.2	1.30	49.4	1.18	66.6
0.05	0.92	18.4	0.79	25.1	0.68	34.8
0.10	0.52	15.3	0.44	18.2	0.38	26.6
0.20	0.40	12.2	0.32	14.0	0.28	19.5
0.50	0.18	7.6	0.15	9.4	0.12	11.2
1.00	0.10	6.3	0.078	7.2	0.065	8.4
2.00	0.03	5.6	0.023	6.2	0.018	7.0

^a $A_{2,\text{net}} = A_{2,\text{net}}^* \times 10^{-3} \text{ cm}^3 \text{ mol g}^{-2}$.

^b $A_{3,\text{net}} = A_{3,\text{net}}^* \times 10^{-3} \text{ cm}^6 \text{ mol g}^{-3}$.

and 1.22×10^6 Da. Only one kind of counterion, Na, was used so that Θ_2 is zero in eq 2.

First, it is seen that the Θ_1 -values are independent on the molar mass used within the experimental error of 5%. This result is in accord with the predictions of Manning's counterion theory. But note, Manning's calculations³ refer to the limit of small ionic strength, *i.e.*, to the range from $C_s = 0$ M to $C_{\max} = 24.3 \times (\xi(b_{\text{brute}}/b_0)^3)^{-1} \text{ mol l}^{-1}$. Here, ξ is 2.40 for $M_{w,\text{brute}} = 3.20 \times 10^5$ Da and 2.74 for the two other PSS-samples. $C_{\max}$ is thus 0.375 and 0.505 M, respectively. The actual ionic strength, on the other hand, ranges from $I = 0.005$ M to 2 M.

Additionally, it should be pointed out that for $I = 0$ the maximal degree of counterion condensation, $\Theta_{1,\max}$, is given by

$$\Theta_{1,\max} = 1/(1 - \xi^{-1}) \quad (4)$$

For $\xi = 2.40$ this leads to $\Theta_{1,\max} = 0.58$ and for $\xi = 2.74$, $\Theta_{1,\max}$ is 0.635. That is, the Θ_1 -values that refer to the lower degree of sulfonation should be somewhat smaller than those referring to the larger one. Table III shows that this is indeed the case. In conclusion, the experiment is again in line with the theory.

Next, it is instructive to examine the molar mass dependencies of $\langle S^2 \rangle_z^{1/2}$, $A_{2,\text{net}}$, and $A_{3,\text{net}}$. These can be well represented by power laws of the type

$$\langle S^2 \rangle_z^{1/2} = K_{\langle S \rangle_z} \cdot M_{w,\text{net}}^{\nu_{\langle S \rangle_z}} \quad (5)$$

$$A_{2,\text{net}} = K_{A_{2,\text{net}}} \cdot M_{w,\text{net}}^{\nu_{A_2}} \quad (6)$$

and

$$A_{3,\text{net}} = K_{A_{3,\text{net}}} \cdot M_{w,\text{net}}^{\nu_{A_3}} \quad (7)$$

The exponents, $\nu_{\langle S \rangle_z}$, ν_{A_2} , and ν_{A_3} are collected in Table V together with the term $2\nu_{A_2} + 1$. They decrease with increasing ionic strength, I . $\nu_{\langle S \rangle_z}$ and ν_{A_3} are always positive, while ν_{A_2} is negative.

According to the theory,¹⁵ $\nu_{\langle S \rangle_z}$ should be in the order of 0.6 for good solvents and 0.5 for the Θ -state ($A_2 = 0$). For good solvents ν_{A_2} should be in the order of -0.2 and ν_{A_2} should decrease when the solvent becomes poorer. Indeed, both predictions are in line with the experiment. It is thus confirmed: (1) for polyelectrolytes the solvent becomes poorer as the ionic strength is raised and (2) the Θ -state will be reached, if at all, at very high salt concentrations.

The theory of nonionic polymers predicts that A_3 is proportional to $A_2^2 M_w$. That is, ν_{A_2} should be equal to $2\nu_{A_2} + 1$. This seems, however, not to be the case as can be seen from Table V. $2\nu_{A_2} + 1$ is significantly larger than ν_{A_3} ; but an explanation cannot be given yet.

Correlations between $\langle S^2 \rangle_z^{1/2}$ and $Z_{e,\text{net}}$

The values of Θ_1 and Θ_2 , listed in Table I, can be used to calculate the net number of the total charges per PSS-polyion, $Z_{e,\text{net}}$. It holds:

Table V. Scaling parameters^a

I/M	0.005	0.01	0.02	0.05	0.10	0.20	0.50	1.00	2.00
$\nu_{\langle S \rangle_z}$	0.612 (0.645)	0.614 (0.644)	0.586 (0.618)	0.549 (0.577)	0.533 (0.561)	0.524 (0.550)	0.490 (0.515)	0.476 (0.499)	0.475 (0.496)
ν_{A_2}	-0.146 (-0.154)	-0.162 (-0.170)	-0.178 (-0.187)	-0.221 (-0.233)	-0.231 (-0.243)	-0.266 (-0.280)	-0.295 (-0.311)	-0.320 (-0.336)	-0.378 (-0.395)
ν_{A_3}	0.625 (0.658)	0.635 (0.666)	0.538 (0.567)	0.465 (0.491)	0.393 (0.416)	0.333 (0.352)	0.286 (0.301)	0.210 (0.221)	0.163 (0.171)
$2\nu_{A_2} + 1$	0.708 (0.692)	0.676 (0.660)	0.644 (0.626)	0.558 (0.534)	0.538 (0.514)	0.468 (0.440)	0.410 (0.378)	0.360 (0.328)	0.244 (0.210)

^a The numbers in parenthesis are obtained when M_w in eqs 5 to 7 is replaced by the weight average degree of polymerization, $\langle P \rangle_w$.

Figure 2. Correlations between $\langle S^2 \rangle_{z,\text{net}}^{1/2}$ and $Z_{e,\text{net}}$.

$$Z_{e,\text{net}} = \delta \langle P \rangle (1 - \Theta_1 - 2\Theta_2), \quad (3)$$

where in the absence of divalent counterions Θ_2 is zero. Some values for $Z_{e,\text{net}}$ are given in Table II.

Figure 2 shows a plot of the radius of gyration, $\langle S^2 \rangle_{z,\text{net}}^{1/2}$ vs. $Z_{e,\text{net}}$. It is seen that the data points form a composite curve irrespective whether they are related to the system PSS/Pb/H or to PSS/Na. Consequently, $\langle S^2 \rangle_{z,\text{net}}^{1/2}$ is predominantly influenced by $Z_{e,\text{net}}$ and only indirectly by other factors such as the temperature and the type of the counterions. However, it must be proved whether this behavior is a general one.

Intramolecular Interactions

First, we define the intramolecular expansion factor, α . This is given by

$$\alpha^2 = \langle S^2 \rangle_z / \langle S^2 \rangle_{z,\theta}, \quad (8)$$

where $\langle S^2 \rangle_{z,\theta}^{1/2}$ and $\langle S^2 \rangle_z^{1/2}$ are the radii of gyration at the θ - and the non θ -state. Note, at the θ -state the polymers are unperturbed by intra- and intermolecular segmental interactions ($\alpha=1$), while in the non θ -state they are perturbed by the excluded volume effect.⁴ Experimentally, the θ -state is given by the

Table VI. Theta-radii of gyration

$M_{w,\text{brute}}/10^5 \text{ Da}$	3.20	7.28	12.2
$\langle S^2 \rangle_{z,\theta}^{1/2}$	27	38	50

condition $A_{2,\text{net}}=0$. The excluded volume, β , is then zero, and hence, $\langle S^2 \rangle_{z,\theta}$ is proportional to $\langle P \rangle_w$, i.e., $v_{\langle S \rangle_z}=0.5$.

For polyelectrolytes¹⁶, the θ -state can be estimated best by plots of A_2 ($A_{2,\text{net}}$) vs. the reciprocal square root of the ionic strength, I . The reason is that such plots yield straight lines at sufficient small $\sqrt{I}$. Thus, it is no problem to determine the ionic strength, I_θ , at which $A_{2,\text{net}}$ becomes zero. An example is given in ref 2.

The θ -radius of gyration, $\langle S^2 \rangle_{z,\theta}^{1/2}$, can be determined, in principle, by light scattering measurements at I_θ . Unfortunately, for polyelectrolytes θ -solvents are electrolyte solutions of very high salt concentration, i.e., in the order of 1 to 5 mol l⁻¹. Since polyions begin to precipitate at such high I_θ -values, light scattering measurements are extremely difficult if not impossible. In general, we are therefore depending on extrapolated values of $\langle S^2 \rangle_{z,\theta}^{1/2}$. These are sensitive to the extrapolation procedure used. Here, a third polynomial fit of $\langle S^2 \rangle_z^{1/2}$ vs. $\ln[I]$ was applied, where $\langle S^2 \rangle_{z,\theta}^{1/2}$ was taken at $\ln[I_\theta]$. The results obtained are summarized in Table VI.

At this point, it should be pointed out that polyions are not uncharged at the θ -state. This is because the excluded volume, β , can be divided in a nonionic term β_0 and an ionic term β_{el} . The nonionic term is in general negative since water is a very poor solvent for the polyion backbones, while β_{el} is positive due to the electrostatic repulsion between the segments. That is, at the θ -state, where $\beta=0$, β_{el} must be positive to compensate the negative value of β_0 .

Our results seem to confirm this fact. The degrees of counterion condensation, Θ_1 and Θ_2 , are always smaller than one, also at very

high I . $\Theta_{1,\theta}$ can be estimated to be in the order of 0.90 to 0.95. That is, between 5 and 10% of the polyon groups remain unneutralized at the Θ -state.

Several authors^{5,17-21} have developed several theories on the expansion factor, α . However, it is common to all these theories that they can be expressed in formulas, which contain only two parameters. These are α and z_{el} , where z_{el} is the electrostatic part of the excluded volume parameter z .

Typical expressions for $\alpha(z_{el})$ are those of:

- (1) Katchalsky and Lifson¹⁷

$$\alpha - 1/\alpha = 1.45 \times z_{el,1} \quad (9)$$

- (2) Ptitsyn¹⁸

$$\alpha^2 = \frac{1}{5.12} [4.12 + (1 + 9.79 \times z_{el,1})^{2/3}] \quad (10)$$

- (3) Alexandrowicz¹⁹

$$\alpha^2 = 1.7 \times z_{el,1}^{0.5} + 0.35 \quad (11)$$

- (4) Fixman⁵

$$\alpha^3 - 1 = 1.91 \times z_{el,2} \quad (12)$$

- (5) Flory²⁰

$$\alpha^5 - \alpha^3 = 2.6 \times z_{el,1} \quad (13)$$

- (6) Hermans²¹

$$\alpha^5 - \alpha^3 = 7.0 \times z_{el,1} \quad (14)$$

First we see, eq 9 to 14 involve α raised to various powers. Equation 9 is of the α^1 -type, eq 10 is of the α^3 -type ($\alpha^2 \sim z_{el}^{2/3}$ or $\alpha^3 \sim z_{el}$), eq 11 is of the α^4 -type ($\alpha^2 \sim z_{el}^{1/2}$ or $\alpha^4 \sim z_{el}$), eq 12 is of the α^3 -type, and eq 13 and 14 are of the α^5 -type. Second, we have to distinguish between two types of z_{el} , namely $z_{el,1}$ and $z_{el,2}$. For 1:1 valence salts, they are given by

$$z_{el,1} = 2.74 \times 10^{-22} \langle P^2 \rangle (1/\langle h^2 \rangle_\theta)^{1.5} (\Theta_e^2/C_1) \quad (15)$$

and

$$z_{el,2} = 7.94 \times 10^{-9} \langle P \rangle (1/\langle h \rangle_\theta) (\Theta_e/C_1^{0.5}), \quad (16)$$

where $\langle P \rangle$ is the average degree of polymerisa-

tion, $\langle h \rangle_\theta$ the mean end-to-end distance at the Θ -state, and C_1 the molar concentration of the added salt. Θ_e is the degree of ionization, *i.e.*, $\Theta_e = 1 - \Theta_1$.

The provement of eq 9 to 16 is complicated by the fact that the nonelectrostatic part of the free energy, F_0 , is assumed to be negligible compared with the electrostatic part, F_{el} . In eq 9 to 16, α is therefore identical with the electrostatic part, α_{el} , of the expansion factor, while the α -values measured include both nonionic and ionic amounts.

Nagasawa *et al.*^{6,22} solved this problem by introducing the half empirical expression

$$\alpha_{\eta,el}^3 = \alpha_\eta^3 - \lim_{c_1 \rightarrow \infty} (\alpha_\eta^3 - 1), \quad (17)$$

where α_η is the experimental expansion factor estimated from intrinsic viscosity data. $\alpha_{\eta,el}$ is then set equal to α_{el} and the left hand sides of eq 9 to 14 are plotted *vs.* $(M_w/C_1)^{0.5}$ and $M_w^{0.5}/C_1$, respectively. Note, $\langle h \rangle_\theta$ is proportional to $M_w^{0.5}$, so that $z_{el,1}$ is proportional to $M_w^{0.5}/C_1$ and $z_{el,2}$ to $(M_w/C_1)^{0.5}$. That is, these plots give straight lines in proportion as whether the experimental data are better described by $z_{el,1}$ or $z_{el,2}$.

Indeed, this procedure is successful.²³ For small M_w it is found that plots of α^3 *vs.* $(M_w/C_1)^{0.5}$ give straight lines, suggesting that z_{el} is identical with $z_{el,2}$. For molar masses of a few millions it seems, on the other hand, that $z_{el,1}$ describes the experiment best. In both cases, the prefactors found for $z_{el,1}$ and $z_{el,2}$ are, however, not in accord with those predicted by the theories, *i.e.*, with 2.60 or 1.91. The reason is not clear yet, but it seems that $\alpha_{\eta,el}$ has not exactly the same meaning as α_{el} . As proposed by Yamakawa²⁴ the relationship

$$\alpha_{el} = \alpha_{\eta,el}^{0.81} \quad (18)$$

may hold.

The above handling is, however, only reasonable in cases where the degree of ionization is a constant, *i.e.*, when Θ_e is independent on C_1 . This is not the case for the present PSS-data. We restrain our analysis therefore

Figure 3. Plots of α_{el} vs. $z_{el,1}$. (1) Ptitsyn, (2) Katchalsky, (3) Hermans, (4) Alexandrowicz, (5) Flory, and (6) experiment. Symbols as in Figure 7.

Figure 4. Plots of α_{el} vs. $z_{el,2}$. (1) Fixman, (2) experiment, and (3) experiment according to Manning. Symbols as in Figure 7.

to the discussion of only two figures.

In Figure 3, α_{el} is plotted vs. $z_{el,1}$ and Figure 4 represents a plot of α_{el} vs. $z_{el,2}$. The curves that represent the different theories were calculated iteratively from eq 9 to 14. The experimental data are the overall expansion coefficients α , where $z_{el,1}$ and $z_{el,2}$ were determined by eq 15 and 16 using for $\langle h^2 \rangle_\theta$ the relation

$$\langle h^2 \rangle_\theta = 6 \times \langle S^2 \rangle_\theta \quad (19)$$

That is, a direct comparison between theory and experiment is not possible, since $\alpha \neq \alpha_{el}$.

However, due to eq 17 it can be expected that α_{el} is smaller than α . The correct experimental α_{el} vs. z_{el} curves will be therefore lie somewhat below those drawn in Figures 3 and 4. That is, in conclusion, none of the present theories is able to describe the experimental data satisfactory. It is interesting, on the other hand, that the data points form composite curves, irrespective which molar mass, degree of sulfonation, or ionic strength is used. This indicates that there is indeed a relationship between α_{el} and z_{el} , but at the moment it cannot be decided whether this is of the α^3 or of the α^5 -type.

The α^1 - or α^2 -type can also not be excluded totally. This is seen from curve 3 in Figure 4. Fixman⁵ assumed that inside a polyion coil the counterion concentration is much higher than that of the added salt due to the effect that some counterions are bound. He, therefore, suggested that the dielectric constant, ϵ , inside the polymer domain should be adjusted to fit the calculated values to the experimental data in order to take into account the effective interactions between counterions and polyion-segments. Here, in principle, this can be made by choosing C_1 in eq 16 appropriately. It is, however, more instructive to insert a theoretical value for C_1 . The appropriate value is, according to Manning³, the maximal counterion concentration $C_{1,max} = 24.3 \times (\xi(b_{brute}/b_0)^3)^{-1} \text{ mol l}^{-1}$ given at the polyion surface. That is, we have to set $C_1 = C_{1,max}$ for $C_1 \leq C_{1,max}$ and $C_1 = C_1$ for all higher concentrations. The result is curve 3 in Figure 4. This shows a upward curvature similar to those of curve 2 in Figure 1. That is, the α_{el} vs. z_{el} curve is transformed into one of the α^1 or α^2 -type.

The theories of Fixman and Manning are, however, not consistent. Fixman's theory bases on the model of a spherical polyion having a uniform segment density, while Manning's theory refers to an infinite long rod. However, curve 3 in Figure 4 shows that it is interesting to combine excluded volume with counterion

condensation calculations. Note, only Fixman has tried to unificate these effects and all other attempts fail up to yet.

Intermolecular Interactions

There are, roughly speaking, two groups of theories on the excluded volume parameter z for linear polymers. One is the theory of the expansion factor, α , just discussed before. It describes the intramolecular interactions, *i.e.*, interactions that act between segments belonging to the same polymer molecule. The other group deals with the intermolecular interactions, *i.e.*, interactions that act between segments of different macromolecules. The central function of these theories is the interpenetration function, Ψ . This is defined by⁴

$$\Psi = (A_2 \cdot M_w^2) / (4\pi^{3/2} \cdot N_A \cdot \langle S^2 \rangle_z^{2/3}), \quad (20)$$

where N_A is Avogadro's number.

Theoretical expressions for Ψ are, in general, represented in the form

$$\Psi = \bar{z} \cdot h(\bar{z}) \quad (21)$$

with $\bar{z} = z/\bar{\alpha}^3$. Here z is the excluded volume parameter, and $h(\bar{z})$ is the excluded volume function. $\bar{\alpha}$ describes the intramolecular expansion of a macromolecule, which is produced by the intermolecular segmental interactions. We call $\bar{\alpha}$ therefore the "intermolecular" expansion factor. Note, α is the "true" intramolecular expansion factor. It describes the expansion of a macromolecule in the absence of intermolecular interaction, *i.e.*, the expansion of an isolated molecule at infinite dilution.

A summary of some of the most important expressions for Ψ is given below.

- (1) Flory, Krigbaum, and Orofino⁴

$$\Psi = \ln(1 + 2.30 \bar{z}) / 2.30 \quad (22)$$

- (2) Yamakawa⁴

$$\Psi = 0.55 \cdot (1 - (1 + 3.90 \bar{z})^{-0.47}) \quad (23)$$

- (3) Casassa and Markovitz²⁵

$$\Psi = (1 - 2^{-5.73\bar{z}}) / 5.73 \quad (24)$$

- (4) Stockmayer²⁶

$$\Psi = \bar{z} / (1 + 2.865 \bar{z}) \quad (25)$$

- (5) Kurata²⁷

$$\Psi = [1 - (1 + 0.683 \bar{z})] / 5.047 \quad (26)$$

However, to test these formulas, *e.g.*, by plots of Ψ vs. $\bar{z}$, a number of problems must be solved before. First, Ψ can be determined experimentally without any ambiguity, but $\bar{z}$ is, in general, unknown. This is mainly due to the fact that in eq 21 $\bar{\alpha}$ is the "intermolecular" expansion factor, while the experimentally accessible expansion factor, α , is the intramolecular one. That is, it is not allowed to calculate z from one of the theories of $\alpha(z)$ and after that to set $\bar{z} = z/\alpha^3$. To do this, *i.e.*, to combine one of the eq 9—14 with one of the eq 22—26, it must be taken sure that the appertaining theories are consistent. Here, only one combination is consistent, namely that of eq 13 with eq 22. All other combinations are more or less inconsistent.

The second problem is that eq 22 to 26 hold exactly only for nonionic linear polymers. It can be shown, however, that the electrostatic expressions of Ψ become equal to those of eq 22 to 26 with the exception that $\bar{z}$ has to be replaced by $\bar{z}_{el,1}$ or $\bar{z}_{el,2}$, respectively. This is achieved by (1) neglecting the intrinsic intermolecular excluded volume effects and (2) by making the same approximations as those leading to eq 9—14. Indeed, this idea is helpful, but it still remains the problem of the correct choice of $\bar{z}_{el,1}$ or $\bar{z}_{el,2}$.

It is seen, the excluded volume concept is somewhat dubious and unsatisfactory. Our analysis is therefore short and simple.

Figure 5 shows plots of Ψ vs. α^3 . The experimental data refer to the different molar masses and α is the measured intramolecular expansion factor. Curves (1) and (2) were calculated using the Casassa–Markovitz theory. In curve (1) eq 24 was combined with eq

Figure 5. Plots of Ψ vs. α^3 . (1) Casassa–Markovitz/Flory, (2) Combination of the Casassa–Markovitz with the Hermans theory. The open symbols refer to PSS, and the closed to Calf-Thymus DNA.

13, the original Flory theory, and curve (2) represents the combination of eq 24 with eq 14, the Hermans theory. Note, both combinations are more or less inconsistent, but curve (2) seems to describe the experiment.

For small α^3 all data points form a composite curve which is close to combination (2). With increasing α^3 the interpenetration function, Ψ , decays, however, into three separate branches, one for each molar mass, $M_{w,brute}$. At a given α^3 -value, Ψ is largest for the lowest molar mass, indicating that excluded volume effects are more significant for short than for long polyion chains.

Figure 5 contains also some experimental data obtained for Calf-Thymus DNA of $M_w = 6.0 \times 10^6$ Da. Interestingly, at small α^3 the DNA data³⁴ follow those of PSS, and at large α^3 they seem to converge to curve (1) or (2). This suggests that it may be possible to describe the excluded volume effects appertaining to different types of polyelectrolytes by one and the same universal interpenetration function, Ψ .

At the moment, however, none of the present

Figure 6. Plots of Ψ vs. z_{el}/α^3 . (1) Yamakawa, (2) experiment with $z_{el} = z_{el,2}$, (3) Casassa–Markovitz, and (4) experiment with $z_{el} = z_{el,1}$.

expressions for Ψ is able to fulfill this task. This is seen from Figure 6, where Ψ is plotted vs. $\bar{z}_{el} = z_{el}/\alpha^3$. Curves (1) and (3) represent the theories of Yamakawa and Casassa–Markovitz. Curves (2) and (4) are the results of the experiment, where in curve (2) z_{el} was calculated by $z_{el,2}$ and in curve (4) by $z_{el,1}$. Note, curve (4) does not converge against curve (3), although Figure 6 could commit this impression. The reason is that $z_{el,1}$ is larger than $z_{el,2}$. Curve (4) is thus expanded over a larger interval of $\bar{z}_{el}$ compared to that of curve (3).

The most striking feature of Figure 6 is, in contradiction to Figure 5, that now all data points of Ψ lie on a single composite curve, irrespective whether they refer to a low or a high molar mass. That is, in conclusion, two parameters are indeed enough to describe the excluded volume effects of polyions. They are z_{el} and α .

A confirmation of this hypothesis is obtained by Figures 7 and 8. In Figure 7, α is plotted vs. the degree of polyion dissociation, Θ_e . Similar to Figure 5, three separate curves are obtained, one for each molar mass. Figure 8

Figure 7. Correlations between the expansion factor, α , and the degree of dissociation, θ_e .

Figure 8. Plot of $z_{el,2}/\alpha^3$ vs. θ_e . Symbols as in Figure 7.

shows, on the other hand, a plot of $z_{el,2}/\alpha^3$ vs. θ_e . Now, in analogy to Figure 6, we observe a single composite curve. Note, this curve is sigmoidal, indicating that excluded volume and dissociation effects are anticooperatively coupled, as expected.

Correlations between A_2 and A_3

Investigations on the third virial coefficient, A_3 , are very few in number compared to the

numerous theories of the second virial coefficient, A_2 . Nevertheless some knowledge on A_3 is required for the accurate evaluation of M_w and A_2 , especially in the case of high-molar-mass polyelectrolytes in good solvents.

One of the first investigations was done by Flory and Krigbaum²⁸ which simply assumed that A_3 has the same relation to A_2 as in the case of rigid sphere molecules; that is

$$A_3/(A_2^2 \cdot M_w) = 5/8 \quad (27)$$

Subsequently, smoothed-density theories of A_3 were developed by Stockmayer and Casassa,²⁹ and by Koyama.³⁰ An approximate closed expression for A_3 was firstly given by Yamakawa³¹; that is

$$A_3/(A_2^2 \cdot M_w) = 4/3 (1 - \exp(-1.664 \cdot \bar{z})) \quad (28)$$

with $\bar{z} = z/\bar{\alpha}^3$, where $\bar{\alpha}$ is again the "inter-molecular" expansion factor.

The latest approximation of the third virial coefficient is given by the renormalization group theory,³² that is

$$A_3/(A_2^2 \cdot M_w) = 0.277 \left[\frac{(32 \cdot \bar{z}/3)}{1 + (32 \cdot \bar{z}/3)} \right]; \bar{z} \leq 0.15 \quad (29)$$

where eq 29 can be extended to the intermediate $\bar{z}$ regime of $0.15 \leq \bar{z} \leq 0.75$. For larger $\bar{z}$ eq 29 approaches the asymptotic good solvent limit

$$A_3/(A_2^2 \cdot M_w) = 0.277 \quad (30)$$

It is common to all these theories that both A_3 and A_2 are zero at the θ -state. The asymptotic values of the ratios $A_3/(A_2^2 \cdot M_w)$ are, on the other hand, quite different. We note that Koyama³⁰ obtained the value of 0.704 and Yamakawa³¹ the value of 1.323. Experimental data of A_3 are, however, rare. Kniewske and Kulicke³³ obtained for the system Polystyrene/Toluene the asymptotic value 0.30.

At this point, it should be noted that eq 27 to 30 were derived for nonionic polymers. Up to now there exists no theory of A_3 for polyelectrolytes. Therefore, we assume that eq 27 to 30 are applicable to polyelectrolytes if the

Figure 9. Plots of $A_{3,net}/(A_{2,net}^2 \cdot M_{w,net})$ vs. $z_{el,2}/\alpha^3$. (1) Yamakawa, (2) rigid sphere, and (3) renormalization group theory. Symbols as in Figure 7.

parameter z is replaced by its electrostatic part z_{el} . This idea is in analogy to the theories of α and Ψ . However, it must be proved in detail.

Typical plots of $A_{3,net}/(A_{2,net}^2 \cdot M_{w,net})$ vs. z_{el}/α^3 are shown in Figure 9. The symbols refer to the case that $z_{el} = z_{el,2}$. Circles stand for $M_{w,brute} = 3.20 \times 10^5$ Da, squares for 7.28×10^5 Da, and triangles for 1.22×10^6 Da. Note, $\bar{\alpha}$ is again set equal to α .

The data of Figure 9 form a composite curve, irrespective which molar mass is used. However, the form of the curve does not agree at all with the theoretical predictions. The most striking feature is that the experimental data of $A_{3,net}/(A_{2,net}^2 \cdot M_{w,net})$ diverge to infinity at $z_{el,2}/\alpha^3 = 0$, while the theoretical converge to zero. The reason for this discrepancy is clear. Experimentally, it is found that A_3 is finite at $A_2 = 0$ (at $z_{el,2}/\alpha^3 = 0$), whereas theory predicts $A_3 = 0$.

Two consequences are deductible from these observations. First, for polyelectrolytes it may be not allowed to define the Θ -state by $A_2 = 0$. It may be more reasonable to define the Θ -state by the condition

Figure 10. Correlations between $A_{3,net}$ and $A_{2,net}^2 \cdot M_{w,net}$.

$$2A_2C + 3A_3C^2 = 0 \quad (31)$$

For $C \neq 0$ this leads to

$$C_\Theta = -2A_2/3A_3, \quad (32)$$

where C_Θ is the concentration which fulfills eq 31. Since C_Θ is positive, either A_2 or A_3 must be negative. For PSS it holds: $A_2 < 0$ and $A_3 > 0$.

Double and triple contacts between macromolecules are, on the other hand, different interactions, and even in nonionic polymer solutions $A_3 \neq 0$ at $A_2 = 0$. It is therefore not unreasonable to define the Θ -state at $A_2 = 0$ like the Boyle temperature for the real gas, even if there are difficulties in the experiments. However, the future will show which is the best definition of the Θ -state.

Second, the nonionic excluded volume theories for A_3 cannot be applied to polyelectrolytes. The experimental and theoretical curvatures are too different. However, there is some light at the horizon. A plot of $A_{3,net}$ vs. $A_{2,net}^2 \cdot M_{w,net}$ gives a single composite curve for all M_w , see Figure 10. Note, similar curves are obtained for DNA, PAA, and other polyelectrolytes.³⁴ In conclusion, $A_{3,net}$ is a simple function of $A_{2,net}^2 \cdot M_{w,net}$. The only problem

that remains, is to find the corresponding theory.

The Post-Zimm Theory

Using the Flory-Huggins lattice model,³⁵ Post and Zimm⁷ derived the following expression for the free energy of mixing for a single polymer molecule with solvent:

$$\frac{\Delta G}{kT} = \frac{V_p}{V_1} \left((\chi - 1) + \frac{A_2^* \omega}{2^{1.5} \alpha^3} + \frac{A_3^* \omega^2}{2 \times 3^{1.5} \alpha^6} \right) + \frac{3(\alpha^2 - 1)}{2} - \ln \alpha^3 \quad (33)$$

where $\omega = (3/\pi^{0.5} \langle h \rangle_\Theta)^3 V_p$. V_1 and V_p are the molecular volumes of the solvent and the polymer, respectively. χ is the Flory-Huggins parameter.²¹

ΔG denotes the change in the free energy on formation of unlike first-neighbor contacts with the loss of solvent-solvent and segment-segment contacts. A_2^* and A_3^* are the second and the third virial coefficients. The asterics indicate that A_2^* and A_3^* are dimensionless. For a comparison with the experiment, A_2^* must be multiplied with $\bar{v}_p^2/v_1$ and A_3^* with $\bar{v}_p^3/v_1$, where $\bar{v}_p$ is the partial specific volume of the polymer, and v_1 the partial molar volume of the solvent. The latter can be easily obtained from density measurements. See, for instance, ref 36.

A_2^* and A_3^* can be expressed in terms of the Flory-Huggins parameter, χ , and the lattice coordination number, q . It holds

$$A_2^* = 0.5 - \chi \quad (34)$$

and

$$A_3^* = 1/3 (1 + 12\chi^2/q - 16\chi^3/q^2) \quad (35)$$

At the conventional Θ -state χ is 0.5 and A_3^* is larger than zero. The Post-Zimm theory⁷ is therefore an attractive one to describe the thermodynamic behavior of polyelectrolytes. However, note the Flory-Huggins lattice theory²¹ was derived for nonionic polymer solutions at high concentration. A sufficient accord between theory⁷ and experiment can be

therefore expected only near the Θ -state, where the local polyelectrolyte-segment concentration is high and the polyelectrolyte charge small.

To calculate A_2^* and A_3^* the parameters χ and q must be known. These are related to the experimentally accessible expansion factor $\alpha = \bar{\alpha}$. It holds⁷:

$$\alpha^8 - \alpha^6 - 2.60 \cdot A \cdot \alpha^3 = B \quad (36)$$

$$A = A_2^* \cdot (3/\pi)^{1.5} (V_p/V_1)^{0.5} \omega^3 / 2^{0.5} \quad (37)$$

$$B = A_3^* (3V_p/\pi \langle h^2 \rangle_\Theta V_1^{1/3})^3 \times 3^{1.5} \quad (38)$$

The molecular volumes V_p and V_1 can be estimated by the relationships $V_p = \bar{v}_p \cdot M_p/N_A$ and $V_1 = \bar{v}_1 \cdot M_1/N_A$, respectively. Note, M_p and M_1 are the molar masses of the polymer and the solvent.

That is, M_p is $M_{w,net}$ and $M_1 = w \cdot M_{H_2O} + [1 - w] \cdot M_{salt}$, where w is the mass fraction of H_2O in the solvent. Typical values obtained for V_p are listed in Table IV. They refer to the system PSS/Pb/H — $M_{w,brute} = 3.20 \times 10^5$ Da.

Two fit-parameters remain in eq 34 to 38, namely χ and q . The lattice-coordination number, q , is believed to be a constant over the whole range of α . The Huggins-parameter, χ , should be change, on the other hand, from $\chi \geq 1/2$ for poor solvents ($\alpha \leq 1$) to values of $\chi < 1/2$ for good solvents ($\alpha > 1$). q can be therefore fixed and χ can be calculated iteratively from measured α -values using eq 36. The χ -values obtained will be then inserted into eq 34 and 35. This yields values for A_2^* and A_3^* . The latter will be transformed into $A_{2,net}$ and $A_{3,net}$ and after that compared with the experiment.

Some typical results obtained by this procedure are given in Table VII. Note, q was set three, which may be the most likely value for q .

We see, χ increases continually with decreasing degree of polyion dissociation, Θ_e . Simultaneously, A_2^* decreases from positive to negative values, while A_3^* converges to the limit of 0.186. That is, χ is smaller than 0.5, if the

Table VII. Predictions of the Post-Zimm theory concerning the system PSS/Pb/H

Θ_e^a	V_p	χ	A_2^*	A_3^*	$A_{2,\text{net}}^b \times 10^3$	$A_{3,\text{net}}^b \times 10^3$
	nm ³				cm ³ mol g ⁻²	cm ⁶ mol g ⁻³
0.38	32.9	0.179	0.321	0.298	9.80	6.73
0.37	35.6	0.301	0.199	0.254	6.08	5.74
0.35	37.6	0.381	0.119	0.225	3.63	5.08
0.33	39.5	0.449	0.051	0.203	1.56	4.59
0.30	41.6	0.477	0.023	0.194	0.70	4.38
0.29	42.6	0.483	0.016	0.192	0.49	4.34
0.27	43.2	0.492	0.0079	0.190	0.24	4.29
0.26	43.8	0.496	0.0036	0.189	0.11	4.27
0.25	44.6	0.498	0.0017	0.188	0.05	4.25
0.16	46.9	0.502	-0.0020	0.187	-0.06	4.23

^a $\Theta_e = 1 - \Theta_1 - 2\Theta_2$.^b $q = 3$. **Figure 11.** Plots of $A_{3,\text{net}}$ vs. α . (1) experiment; (2) and (3) theory, (2) $q = 12$, (3) $q = 3$.

solvent is good, and χ is larger than 0.5, if the solvent is poor. More interesting is, however, that A_3^* is finite when A_2^* becomes zero. This suggests that triplets of intermolecular segmental interactions are present at $A_2^* = 0$, while doublets are not.

Columns 6 and 7 of Table VII contain the actual theoretical values of $A_{2,\text{net}}$ and $A_{3,\text{net}}$. These are in qualitatively good agreement with the experiment, but the quantitative accord is, however, acceptable only near the Θ -state. This is seen from Figure 11, where $A_{3,\text{net}}$ is plotted vs. α . For small α the theoretical and experimental $A_{3,\text{net}}$ -values are equal within the experimental error. For larger α the experi-

mental $A_{3,\text{net}}$ -values increase strongly, while the theoretical values converge to the limit of $1/3 \bar{v}_p^3/v_1$. In addition, the influence of q on $A_{3,\text{net}}$ is rather small. $A_{3,\text{net}}$ becomes only a little larger as q is raised from 3 to 12.

At this point, it should be pointed out that the Post-Zimm theory gives quantitatively better fits to $A_{2,\text{net}}$ than the theories of Flory-Orofino³⁷ and Mandel-Nicolai,³⁸ discussed in the previous paper.² This is remarkable, because the latter are polyelectrolyte theories, while the Post-Zimm theory is not. The reason is clear. In all present polyelectrolyte theories the effect of $A_{3,\text{net}}$ on $A_{2,\text{net}}$ is neglected.

CONCLUSIONS

The following conclusions can be drawn:

(1) Counterions condense or bind under certain conditions to polyelectrolytes such as poly(styrene sulfonate). The degree of counterion condensation, Θ , can be determined experimentally quite well by dialysis equilibrium experiments or with ion-sensitive electrodes. For PSS, the results agree quite well with the theoretical predictions of Manning. It is found that Θ is dependent on the valence of the counterions, the charge density para-

meter, ξ , and the ionic strength I ; but Θ is independent on the molar mass, M_w , of the polyion.

(2) Due to the effect of counterion condensation it becomes necessary to distinguish between brute and net polyion properties. A net quantity accounts the effect of counterion condensation, while a brute quantity does not. For PSS, it is found that $A_{2,\text{net}}$ and $A_{3,\text{net}}$ are significantly smaller than $A_{2,\text{brute}}$ and $A_{3,\text{brute}}$, while $\langle S^2 \rangle_{z,\text{net}}^{1/2}$ and $\langle S^2 \rangle_{z,\text{brute}}^{1/2}$ are identical. This is mainly due to the fact that the former are quantities describing the concentration dependence of I_{SC} , while $\langle S^2 \rangle_z^{1/2}$ is obtained from the angular dependence of the intensity of the scattered light.

(3) The magnitude of the radius of gyration is predominantly influenced by the total number of nonneutralized charges per polyion. Especially, for PSS we have found that $\langle S^2 \rangle_z^{1/2}$ does not change its magnitude at a fixed value of $Z_{e,\text{net}}$, when one type of counterion is exchanged against another. However, it is not expected that this behavior is a general one. Inter- and intramolecular ion cross-linkings between different polyion segments are thinkable. These would reduce the magnitude of $\langle S^2 \rangle_z^{1/2}$.

(4) The conventional excluded volume theories on α , A_2 , and A_3 developed for nonionic polymers and subsequently modified for polyelectrolytes, are not suited to explain the behavior of PSS- or DNA-polyions in solution. There are a number of absurdities. First, it is not clear at all which parameter of z_{el} should be used, $z_{\text{el},1}$ or $z_{\text{el},2}$? Probably a new z_{el} -parameter must be defined that accounts the exact counterion concentration at the polyion surface. Second, there is some confusion between the intra- and "intermolecular" expansion factors, α and $\bar{\alpha}$. In most cases, α is simply set equal to $\bar{\alpha}$. This is, however, only allowed if the binary cluster integral for segments in the same polymer chain is the same as that for two segments belonging to different chains. Unfortunately, this cri-

terium is fulfilled, if at all, only for two or three combinations of the present intra- and intermolecular excluded volume theories. Third, experimentally it is found that A_3 is finite at $A_2=0$, while the theories predict $A_3=0$. Qualitatively correct predictions are only made by the theory of Post and Zimm. This theory may therefore serve as the starting point for future theories. However, there are some refinements necessary that should include the following points:

(a) Post and Zimm assume a gaussian distribution of segments in both the expanded and the Θ -state. This is unlikely for the configuration of polyelectrolytes; (b) the Post-Zimm model ignores details concerned with the fact that segments of the polymer chain are connected rather than being distributed in spherical shells of uniform density, and (c) the Post-Zimm theory refers to nonionic polymers in solution. That is, all electrostatic effects are neglected up to yet.

(5) Finally, it should be noted that it may be possible to develop a universal excluded volume/counterion condensation theory applicable to all types of polyelectrolytes. This idea bases on the fact that the physicochemical behavior of different polyelectrolytes such as PSS, DNA, and PAA can be described in a uniform manner by functions like Ψ . That is, after solving the problems of α , A_2 , and A_3 the next step should be a unification of the polyelectrolyte theories. All these problems are now under consideration.

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