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Possible Scaling Relations for Semidilute Polyelectrolyte Solutions

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ABSTRACT: With the help of recent polymer scaling theories and the theory of the electrostatic persistence length, scaling relations are formulated for semidilute polyelectrolyte solutions. In the case of added salt, the derivations are straightforward, whereas conjectural assumptions are needed for salt-free polyelectrolyte solutions. Various power laws for the correlation length, radius of a single chain, scattering functions and osmotic pressure are derived, but the formulas usually lack precise numerical coefficients. The theory is applied quantitatively to neutron-scattering data and qualitatively to viscosity measurements. A novel application is a semiquantitative explanation of the strong concentration dependence of the dielectric increment. Simple expressions are found for several empirical dielectric parameters.

Polymer solution theory has advanced considerably in recent years. De Gennes¹ established the remarkable $n = 0$ analogy so that Wilson's renormalization group theory of critical phenomena² could be employed to calculate the polymer excluded volume exponent. Des Cloizeaux³ was able to generalize this result to elucidate the semidilute region, where the chains overlap. Wilson's theory justifies the scaling laws due to Widom^{4,5} and Kadanoff.⁶ Vice versa, a scaling approach has proven fruitful in polymer solution theory.⁷⁻¹⁰ The theoretical results correlate nicely with, for instance, neutron-scattering data.⁸

No satisfactory theory of polyelectrolytes in the absence of salt is available. Because the polyions are greatly extended, polyelectrolyte solutions are semidilute in practice. De Gennes et al.^{11,12} have formulated a tentative scaling theory, but it suffers from several drawbacks: (I) screening due to the counterions is neglected; (II) hence the Coulomb potential has infinite range and the validity of scaling arguments may be seriously questioned; and (III) owing to the long range of the electrostatic potential, even when small-ion screening is present, the persistence length must be renormalized in any adequate theory.^{13,14}

Concerning item III, it is pertinent to remark on two recent papers. Pfeuty¹² summarizes scaling procedures for polyelectrolytes of low charge density, and we will show that any renormalization of the Kuhn length is unnecessary in that case. On the other hand, Kosmas and Freed⁹ try to show that polyelectrolyte theory reduces to polymer theory in a simple way because the range of the interaction is finite. One must apply their result with care. Any potential between segments which is strong enough and has a large enough range will stiffen the chain locally. Kosmas and Freed use a path integral formulation with the explicit assumption that the chain is Gaussian up to a contour distance of the order of the Kuhn length. If the Kuhn length is an invariant as they assume, this supposition clearly breaks down because the local flexibility decreases with increasing interaction strength. In other words, the chain becomes rodlike along contour distances larger than the original Kuhn length. We have recently formulated a theory incorporating this effect within the context of a wormlike chain model.¹⁵

In our discussion of polyelectrolytes without salt, we will adopt the viewpoint that uncondensed counterions screen the polyions appreciably. Hence, if we concern ourselves only with the statistics of the polyions, we may devise a theory analogous to that of polymer solutions provided we allow for a number of suitable modifications. For polyelectrolytes with added salt, this has been done for the dilute region. The basic notions are the existence of an electrostatic persistence length and the concept of local

cylindrical symmetry, and the theory is developed extensively in ref 13-18. Guided by these results, we will formulate scaling relations for semidilute polyelectrolyte solutions. We begin with the case of excess salt, but our emphasis will be on polyelectrolytes without any added salt. In the latter case, we must stress that the results are rather speculative.

Polyelectrolytes with Added Salt

Our solution contains N polyelectrolytes of contour length l within a volume V . We view each polyelectrolyte as a wormlike chain with bare persistence length L_p bearing elementary charges (q_e) which interact via a Debye-Hückel potential with screening length κ^{-1} . On each chain the number of charges is P , and they are separated by a contour distance $A = lP^{-1}$. We call A the segment length, and we will refer to the segments as monomers. The charges stiffen the chain drastically. Quantitatively, this may be expressed by the electrostatic persistence length derived independently by Odijk¹³ and Skolnick and Fixman¹⁴

$$L_e = Q/4\kappa^2 A^2 \quad (1)$$

Here $Q \equiv q_e^2/Dk_B T$ is the Bjerrum length, a natural length scale for polyelectrolyte solutions, D is the dielectric constant of the solvent, and $k_B T$ denotes the Boltzmann factor. In eq 1, counterion condensation is disregarded and $A\kappa \ll 1$. Pfeuty¹² has discussed the small coupling limit $A \geq 3Q$. In practice, the Debye radius is smaller than 300 Å, and the Bjerrum length is equal to 7 Å for water at 25 °C, and so we usually have $40Q\kappa > 1$, i.e., $\kappa L_e < 1$ from eq 1. Thus the range of extra stiffening is within the range of the interaction, and there is spherical symmetry which means Pfeuty's conclusions are correct.

Here we examine the strong coupling limit $A \leq Q$. We then have local cylindrical symmetry.^{15,17,18} Although the theory of counterion condensation has been reanalyzed by a large number of workers,¹⁷⁻²⁵ it will take some time to sort things out. Hence we adopt the theory in its simplest form due to Manning²⁶ and Oosawa.²⁷ If $A \leq Q$, eq 1 is modified to¹⁵

$$L_e = 1/4Q\kappa^2 \quad (2)$$

At this juncture we would like to remark on the validity of eq 1 and 2. In our original derivation of eq 1,¹³ we considered polyelectrolytes near the rod limit so that excluded-volume effects could be neglected, and we viewed the electrostatic interaction as perturbing the interaction associated with the bare persistence length. Thus, arguments based on standard perturbation theory led us to state that L_e should be smaller than L_p for eq 1 to be valid.

(See also eq 20 of ref 15.) However, this condition is too restrictive. In fact, we may expect eq 1 to hold whenever $\kappa L_t \gg 1$, where the total persistence length $L_t = L_p + L_e$. (Note that in ref 13 L_e is derived for $\kappa l \gg 1$, and since $l \leq \frac{1}{2} L_t$ for chains near the rod limit, this also implies $\kappa L_t \gg 1$.) In that case, the only interactions between charges which are important are those pertaining to sections of length equal to κ^{-1} or smaller, i.e., pieces of chain which are extremely stiff. Hence, if $L_e > L_p$, the calculation of the electrostatic persistence length given in ref 13 is still legitimate as long as $\kappa L_t \gg 1$. The alternative procedure due to Skolnick and Fixman¹⁴ supports this assertion; they call the condition $\kappa L_t \gg 1$ the “local stiffness approximation”.

A second problem concerns the relation between the total persistence length and the equivalent segment length. We have argued qualitatively that the segment length should equal $2L_t$ if $\kappa L_t \gg 1$.¹⁵ Bailey gives an approximate quantitative analysis, and we refer the reader to his paper.⁴⁶

In summary, we may state that eq 1 and the segment length derived via eq 1 are valid as long as $\kappa L_t \gg 1$. Equation 1 will still be a reasonable first-order approximation if $\kappa L_t > 1$. If $\kappa L_t < 1$, this approximation becomes very poor.

If $A \leq Q$, Onsager's argument used by Manning²⁶ in his counterion condensation theory is not modified if a wormlike chain model is used instead of a straight line charge.¹⁷ Thus, eq 2 holds, but again we need at least the condition $\kappa L_t > 1$. Note the strong κ dependence of L_e which implies that the condition $\kappa L_t > 1$ is equivalent to $L_p > Q$,¹⁵ i.e., a condition usually met in practice. Moreover, in a lot of cases $\kappa L_t \gg 1$.

Let our solution contain excess 1–1 electrolyte of concentration n . Then the Debye–Hückel parameter is given by

$$\kappa^2 = 8\pi Qn \quad (3)$$

As discussed in ref 15, we may reconsider the polyelectrolytes as wormlike chains with total persistence length $L_t = L_p + L_e$ which are surrounded by an impenetrable radius approximately proportional to κ^{-1} . Since $L_t \gg \kappa^{-1}$, the excluded volume between the renormalized Kuhn segments scales like¹⁵

$$\beta_{el} \simeq L_t^2 \kappa^{-1} \quad (4)$$

(The sign \simeq means equal to within a factor of order unity. Large factors like 16π will be included later on.) Actually we make an error in eq 4 because the cooperative effect of the charges along the chain gives a rather stronger dependence on κ .^{16,28} Nevertheless, these corrections are of order $\ln \kappa$ and of minor importance in deriving scaling relations. Table I of ref 28 supports this assertion.

Via scaling relations, we want to deduce the intensive properties of our system which are independent of the contour length. This implies that we must take the limit of very large l . Thus, the dimension R of the single chain in infinite dilution must approach the Flory limit^{29,30}

$$R_F \simeq l^{1/2} L_t^{1/2} Z_{el}^{1/5} \simeq l^{3/5} L_t^{1/5} \kappa^{-1/5} \quad (5)$$

where Z_{el} is the electrostatic excluded-volume parameter¹⁵

$$Z_{el} \simeq \beta_{el} l^{1/2} L_t^{-7/2} \simeq l^{1/2} \kappa^{-1} L_t^{-3/2} \quad (6)$$

In eq 5, the power dependence of Z_{el} ensures that the excluded-volume exponent has the correct value 0.6.

The following scaling procedure is standard.^{7–10} As we increase the polyelectrolyte concentration, we attain a certain monomer concentration c_+ which defines the onset

of entanglement between the coils.

$$c^+ \simeq l A^{-1} R_F^{-3} \quad (7)$$

We may readily obtain the correlation length ξ by imposing the conditions: (1) $\xi \simeq R_F$ at $c = c^+$ where $c \equiv NP/V$; (2) in the semidilute region ($A^{-3} \gg c \gg c^+$), ξ must scale like a power x of the concentration, $\xi \simeq R_F (c^+/c)^x$; and (3) ξ must be independent of the contour length. From eq 5 and 7, we find $X = 3/4$ and so

$$\xi \simeq R_F (c^+/c)^{3/4} \simeq L_t^{-1/4} \kappa^{1/4} (Ac)^{-3/4} \quad (8)$$

The so-called blob picture gives an appealing interpretation of the correlation length. Each polyelectrolyte chain may be pictured as a Gaussian coil of blobs. Each blob has a radius ξ . Within a blob there is no interference from the other chains, and the g segments of length $2L_t$ exert a full excluded-volume effect.

$$\xi \simeq g^{3/5} L_t^{4/5} \kappa^{-1/5} \quad (9)$$

Parts of the chain which are separated by distances larger than ξ are effectively screened by the presence of the other coils. In the semidilute region, the radius of a single coil can be expressed by

$$R(c) \simeq l^{1/2} L_t^{-1/2} g^{-1/2} \xi \quad (10)$$

With the aid of eq 8 and 9, g can be eliminated.

$$R(c) \simeq l^{1/2} L_t^{1/8} \kappa^{-1/8} (Ac)^{-1/8} \quad (11)$$

Let us write down the relations for the interesting limiting case of large electrostatic persistence length so that the polyelectrolyte effect really dominates. For $L_e \gg L_p$

$$c^+ \simeq l^{-4/5} A^{-1} Q^{3/5} \kappa^{9/5} \quad (12)$$

$$\xi \simeq Q^{1/4} \kappa^{3/4} (Ac)^{-3/4} \quad (13)$$

$$R \simeq l^{1/2} Q^{-1/8} \kappa^{-3/8} (Ac)^{-1/8} \quad (14)$$

There are three restrictions on these equations: (i) we must remain within the semidilute region $A^{-3} \gg c \gg c^+$; (ii) there should be enough Kuhn segments within a blob to ensure a complete excluded-volume effect (if L_p is not too large, this implies $\xi L_e^{-1} \gg 1$, i.e., $c \ll Q^{5/3} \kappa^{11/3} A^{-1}$); and (iii) we must have an excess of salt $n \gg c$. Of course, we could keep κ constant if we dilute the solution isoionically.

Equations 8–14 may be verified by neutron scattering. Measurements of the osmotic pressure are also possible. In the dilute region, the osmotic pressure scales like

$$\pi_p/k_B T \simeq cA/l \quad (15)$$

In the semidilute region, π_p should be independent of l and should scale like a power of c .⁸ From eq 15, we require

$$\pi_p(c^+)/k_B T \simeq c^+ A/l \quad (16)$$

Hence, it follows that for $L_e \gg L_p$

$$\frac{\pi_p}{k_B T} \simeq \frac{c^+ A}{l} \left(\frac{c}{c^+} \right)^{9/4} \simeq \xi^{-3} \simeq A^{9/4} Q^{-3/4} \kappa^{-9/4} c^{9/4} \quad (17)$$

Scaling in the Absence of Salt

The approach is now much more conjectural. To make headway, we introduce two major assumptions, both very difficult to assess: (A) there is no interchain stiffening, only charges on one chain increase the persistence length and the influence of charges on the other coils is neglected; and (B) an assumption due to Weill,³¹ Debye–Hückel screening is caused by uncondensed counterions only ($A \leq Q$)

$$\kappa^2 = 4\pi A c \quad (18)$$

As the Debye length is now dependent on C , scaling becomes more intricate.

We consider two alternatives. (A) (1) At a certain concentration c_1 there corresponds a particular $\kappa(c_1)$ and $L_t(c_1)$. Because the range of the interaction is finite, we have a quasineutral polymer solution, and so the preceding situation obtains. Let us introduce a hypothetical polymer solution with the following characteristics: variable monomer concentration c , constant segment length $\bar{A} = A$, constant screening length $\bar{\kappa}^{-1} = \kappa^{-1}(c_1)$, and constant persistence length $\bar{L}_t = L_t(c_1)$. This solution will have the same intensive properties as our real polyelectrolyte solution only at $\bar{c} = c_1$; for instance, the correlation lengths are equal if $\bar{c} = c_1$, $\xi(\bar{c}, \bar{A}, \bar{\kappa}, \bar{L}_t) = \xi(c_1, A, \kappa, L_{t1})$. The functional dependence of ξ is easy to determine by the scaling procedure outlined earlier (see eq 8).

$$\xi \simeq \bar{L}_t^{-1/4} \bar{\kappa}^{1/4} (\bar{A} \bar{c})^{-3/4} \quad (19)$$

Hence we have

$$\xi(c_1) \simeq L_t^{-1/4}(c_1) \kappa^{1/4}(c_1) (Ac)^{-3/4} \quad (20)$$

At a second concentration c_2 , we compare the real polyelectrolyte solution with a different polymer solution having parameters \bar{c} , $\bar{A} = A$, $\bar{\kappa} = \kappa(c_2)$, $\bar{L}_t = L_t(c_2)$. Again, the two solutions have identical properties only at $\bar{c} = c_2$ and then $\xi(\bar{c}_2) = \xi(c_2)$. Therefore, we again have

$$\xi(c_2) \simeq L_t^{-1/4}(c_2) \kappa^{1/4}(c_2) (Ac_2)^{-3/4} \quad (21)$$

This elaborate process may be visualized for any concentration and it justifies simply inserting eq 18 into eq 8 to obtain $\xi(c)$ for all concentrations.

$$\xi(c) \simeq \left(L_p + \frac{1}{16\pi QAc} \right)^{-1/4} (4\pi Ac)^{1/8} (Ac)^{-3/4} \quad (22)$$

Limiting cases are: for $L_e \ll L_p$

$$\xi \simeq L_p^{-1/4} (Ac)^{-5/8} \quad (23)$$

and for $L_e \gg L_p$

$$\xi \simeq Q^{1/4} (Ac)^{-3/8} \quad (24)$$

Within the semidilute region, the radius of a single chain is given by

$$R(c) \simeq l^{1/2} \left(L_p + \frac{1}{16\pi A Q c} \right)^{1/8} (Ac)^{-3/16} \quad (25)$$

for $L_e \ll L_p$

$$R(c) \simeq l^{1/2} L_p^{1/8} (Ac)^{-3/16} \quad (26)$$

and for $L_e \gg L_p$

$$R(c) \simeq l^{1/2} Q^{-1/8} (Ac)^{-5/16} \quad (27)$$

Again we must require a fully exerted excluded-volume effect within a blob, but we discuss the condition $\xi \gg L_e$ later on. Note that it is impossible to start from the single chain problem using this procedure.

(A) (2) On the other hand, we may view the transition from the dilute to the semidilute region. Evidently, the total persistence length is then equal to

$$L_t \simeq L_e = (16\pi QAc)^{-1} \quad (28)$$

Hence, there is a critical concentration c^* at which the polyelectrolyte starts bending appreciably.

$$l \simeq L_t^* \simeq (16\pi QAc^*)^{-1} \quad (29)$$

Now it is plausible to have a polyion lattice if the polyions are rigid,¹¹ i.e., for $c < c^*$. Thus the critical interrod distance d^* at concentration c^* is

$$d^{*2} l \simeq l / Ac^* \quad (30)$$

Equation 29 yields

$$d^* \simeq (16\pi Ql)^{1/2} \quad (31)$$

The correlation length ξ has a value d^* at $c = c^*$

$$\xi(c^*) \simeq d^* \quad (32)$$

If we employ the usual scaling procedure, ξ independent of l , etc., our result is simply

$$\xi \simeq (Ac)^{-1/2} \quad (c \gg c^*) \quad (33)$$

We require that $L_e \gg \xi$, otherwise another length scale interferes. The chains are clearly Gaussian with

$$R(c) \simeq (l/16\pi QAc)^{1/2} \quad (c \gg c^*) \quad (34)$$

Nevertheless, we do not know whether the coils are locally parallel or more disoriented.

(B) Transition Behavior. In what follows we regard polyelectrolytes with very flexible backbones setting L_p equal to Q for convenience. The transition behavior we discuss will occur in the region where $L_e \gg L_p$.

Equation 22 is valid only if $\xi \gg L_e$, in other words

$$40(\kappa Q)^{5/4} \gg 1 \quad (35)$$

Likewise, in eq 33 it is assumed that $L_e \gg \xi$, i.e.,

$$\kappa Q \ll 1 \quad (36)$$

We may expect a transition to occur at κQ equal to some number γ of order 0.1.

De Gennes³³ has made the following remarks concerning this transition. De Gennes et al.¹¹ have studied the melting of a polyion lattice with interrod distance d . They calculate the mean-square displacement $\langle \delta^2 \rangle$ of the chains

$$\langle \delta^2 \rangle / d^2 \simeq 0.1 Q \kappa \quad (37)$$

Even if the lattice is deformed, eq 37 will still hold as long as the polyions remain locally parallel and as long as $L_e \gg d$. A useful criterion for the melting of a lattice is the Lindemann rule valid for a wide variety of substances;³² melting occurs if the Lindemann ratio $\langle \delta^2 \rangle^{1/2} / d$ exceeds a certain value $\simeq 0.15$. Hence, the polyelectrolyte lattice should melt at concentration c^{**}

$$Q(4\pi Ac^{**})^{1/2} = Q\kappa^{**} \simeq 0.2 = \gamma' \quad (38)$$

Very surprisingly, it turns out that

$$\gamma \simeq \gamma' \quad (39)$$

Therefore, the two entirely different viewpoints are mutually consistent. If $Q\kappa \geq 0.2$, the solution is almost certainly isotropic. In the other case, $Q\kappa < 0.2$, there will probably be some anisotropy, but we do not know its exact nature. Finally, we remark on a restriction on eq 23–27. The contour length must be large enough so that we always have a semidilute solution for $\kappa \gg \kappa^{**}$. We require that $R(c) \gg \xi(c)$, and if we use eq 38, it is easy to show that the restriction is simply that l must be much larger than the Bjerrum length.

We summarize our results in Table I where the exponents α and β are defined by the relations $\xi \sim c^{-\alpha}$ and $R \sim c^{-\beta}$. Typical values of the monomer concentrations are $c^* = 1.8 \times 10^{-3} \text{ mol L}^{-1}$ and $c^{**} = 4 \times 10^{-2} \text{ mol L}^{-1}$ for a polyelectrolyte with $A = 2.5 \text{ \AA}$, $l = 10^3 \text{ \AA}$, and $Q = 7 \text{ \AA}$.

The values of the exponents are to be compared with the De Gennes theory exponents¹¹ $\alpha_G = 1/2$ and $\beta_G = 1/4$. It is clear that there is a large concentration range where there is little difference between the predicted exponents of the two theories. This is extraordinary since the physical

Table I

concn region	α^a	β^a
I, $c \gg (16\pi Q^2 A)^{-1}$	5/8	3/16
II, $0.04(4\pi Q^2 A)^{-1} \approx c^{**} \lesssim c \ll (16\pi Q^2 A)^{-1}$	3/8	5/16
III, $(16\pi Q A l)^{-1} \approx c^* \ll c \ll c^{**}$	1/2	1/2

^a The values of the exponents α and β .

pictures are completely at variance.

(C) Neutron Scattering. Following De Gennes et al.¹¹ and Pfeuty,¹² we briefly describe the single chain scattering function $S_1(q)$ and the many chain scattering function $S(q)$.

(i) In the case $c > c^{**}$, we have

$$S_1(q) \approx 1/qA \quad (qL_t > 1) \quad (40)$$

$$S_1(q) \approx \frac{1}{q^{5/3} A L_t^{2/3}} \quad (\xi^{-1} < q < L_t^{-1}) \quad (41)$$

$$S_1(q) \approx \frac{1}{q^2 A L_t^{2/3} \xi^{1/3}} \quad (R^{-1} < q < \xi^{-1}) \quad (42)$$

(ii) In the other case, $c < c^{**}$, we obtain

$$S_1(q) \approx 1/qA \quad (qL_t > 1) \quad (43)$$

$$S_1(q) \approx 1/Aq^2 L_t \quad (R^{-1} < q < L_t^{-1}) \quad (44)$$

In considering $S(q)$, we confine ourselves to the region $c < c^{**}$ since we do not know the detailed statistics when $c > c^{**}$.

At high values of the scattering vector q , we have $S = S_1$, and so

$$S(q) \approx 1/qA \quad (qL_t > 1) \quad (45)$$

At low values of q

$$S(0) \approx k_B T \frac{dc}{d\pi_p} \quad (46)$$

For the osmotic pressure, eq 17 and 18 yield

$$\pi_p/k_B T \approx 10(Ac^{1/3})^{3/8} c \quad (47)$$

Note the almost linear dependence on the concentration.⁴⁷ It appears that $S(0)$ is of order unity and somewhat smaller than $S(L_t^{-1})$. We therefore expect some maximum to occur, perhaps at $q_m \approx \xi^{-1}$.

Applications

Neutron Scattering. (i) As yet the only measurements of the electrostatic persistence length are the following. Moan and Wolff³⁴ have determined the persistence length of unlabeled carboxymethylcellulose as a function of A at a constant polyelectrolyte concentration. Weill³¹ has pointed out that their result is in semiquantitative agreement with eq 1 and 2. If $A \geq Q$, κ^{-2} will be linear in A , and so from eq 1 we have

$$L_e = \left(\frac{Q}{A}\right) L_{e,A=Q} \quad (48)$$

The predicted A^{-1} dependence agrees with experiment. At $c_p = 8 \times 10^{-3} \text{ g cm}^{-3}$ Moan and Wolff³⁴ find a value of 30 Å for $L_{e,A=Q}$. If we take $Q = 7 \text{ Å}$, then $L_e \approx 40 \text{ Å}$ from eq 1 with $c_1 = 1.5 \times 10^{-2} \text{ mol L}^{-1}$. Nevertheless, this agreement must be checked again. In principle, we expect a very low-scattering intensity at low values of the scattering vector in contrast with Moan and Wolff's results. Perhaps the charge density is too low for a bump to be seen.

(ii) In a recent review,³⁵ Moan et al. give a value of 0.30 for the exponent β . The measurements were performed

Table II

region ^a	concn range	qualitative remarks
A	$c_G^* \gg c$	very dilute; negligible interaction between the polyions
B	$c^* > c \gtrsim c_G^*$	dilute/semidilute; polyions remain rigid and interact strongly
C \equiv III	$c^{**} > c > c^*$	drastic decrease in the viscosity due to large decrease in polyion dimensions
D \equiv I + II	$c_4 > c > c^{**}$	Fuoss law, chain behavior Rouselike ¹¹
E	$c > c_4$	polymer behavior

^a Various concentration regions conjectured for the viscosity.

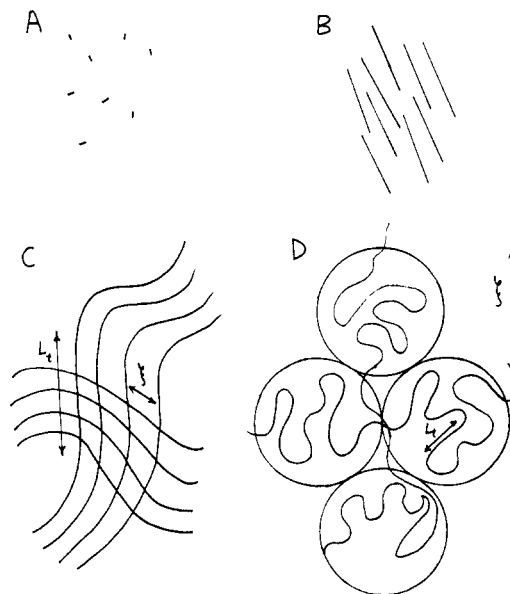


Figure 1. Regions A-D.

in region II with unlabeled chains. This value corresponds quite well with the value $5/16 \approx 0.31$.

Viscosity Measurements. Wolff³⁶ has given a recent review on the viscosity of semidilute polyelectrolyte solutions. He describes five separate regions together with four cross-over concentrations. It is interesting that our discussion predicts at least five regions too.⁴⁸ This is outlined in Table II (our notation differs from Wolff's). Figure 1 may also be useful.

Our model describes the viscosity measurements, at least qualitatively. A last remark concerns region D. The reptation model³⁷ would give a strong l^3 dependence which is not observed experimentally. This might be due to the very high values of l necessary for the onset of entanglement behavior to be observed.³⁸

Dielectric Measurements. We attempt to explain the strong dependence of the dielectric permittivity on the polyelectrolyte concentration. At least two dispersion regions are observed.³⁹ One of the proposed mechanisms is the fluctuation of condensed counterions along the polyelectrolyte backbone.⁴⁰ The dispersion at low frequencies is attributed to fluctuations along the whole chain. The interpretation of the second region is more tenuous. Possibly some kind of potential barriers exist along the chain on a short time scale. In the second dispersion region, counterions fluctuate along a certain average distance b . Since the correlation length ξ measures the mean distance between contact points⁷ in the semi-

dilute solution, we may conjecture that ξ is simply equal to b . This gives a neat physical interpretation of the ad hoc potential barriers postulated by van der Touw and Mandel.

Because the conductivity must be kept low, dielectric measurements on polyelectrolytes are performed in the region $c < c^{**} = 4 \times 10^{-2} \text{ mol L}^{-1}$. The empirical scaling laws for the dielectric increments $\Delta\epsilon_s$ and $\Delta\epsilon_2$ of the first and second regions respectively read:

$$\Delta\epsilon_s/c = (\Delta\epsilon_s/c)_0(1 + B_s c)^{-1} \simeq (\Delta\epsilon_s/c)_0 \frac{1}{B_s c} \quad (c \text{ large}) \quad (49)$$

$$\Delta\epsilon_2/c = (\Delta\epsilon/c)_0(1 + B_2 c)^{-1} \simeq (\Delta\epsilon_2/c)_0 \frac{1}{B_2 c} \quad (c \text{ large}) \quad (50)$$

Here B_s and B_2 are empirical interaction parameters. From linear response arguments, it is expected that $\Delta\epsilon_s$ is proportional to R^2 and ϵ_2 to $b^2 \equiv \xi^2$.

If $c \ll c^{**}$, then from eq 32 and 34, we obtain

$$R^2 \simeq lL_e = l^2 \left(\frac{1}{16\pi QAlc} \right) \quad (51)$$

with

$$\lim_{c \rightarrow c^{**}} R^2 \simeq l^2$$

from which it follows that

$$\Delta\epsilon_s/c \simeq (\Delta\epsilon_s/c)_0 \frac{1}{16\pi QAlc} \quad (52)$$

and hence,

$$B_s \simeq 16\pi QAl \quad (53)$$

In the same way, we have, for the second dispersion region,

$$\xi^2 \simeq d^{*2} \frac{c^*}{c} \simeq d^{*2} \left(\frac{1}{16\pi QAlc} \right) \quad (54)$$

with

$$\lim_{c \rightarrow c^{**}} \xi^2 \simeq d^{*2}$$

so that eq 50 is rewritten as

$$\Delta\epsilon_2/c \simeq (\Delta\epsilon_2/c)_0 \left(\frac{1}{16\pi QAlc} \right) \quad (55)$$

Hence, we conclude that the interaction parameters are equal and are given by

$$B_2 \simeq B_s \simeq 16\pi QAl \quad (56)$$

For a polyelectrolyte (NaPSS) with $l = 1.2 \times 10^3 \text{ \AA}$, $A = 2.5 \text{ \AA}$, and $Q = 7 \text{ \AA}$, we find $B_2 \simeq B_s \simeq 600 \text{ L mol}^{-1}$. Compare this with typical values of B_2 and B_s : 600–2400 L mol^{-1} .³⁹ The correspondence between the values is surprising. Another prediction is that $d^* \simeq b_0$. We obtain $d^* = 500 \text{ \AA}$ in good agreement with the value 400 \AA for b_0 .³⁹

Concluding Remarks

Apparently, some evidence for our crude theory exists. Clearly, many more experiments are necessary to elucidate the structure of semidilute polyelectrolyte solutions.

We have made certain assumptions which some may consider bold. We must bear in mind that these assumptions enable us to derive a number of scaling relations in a straightforward manner. Although scaling is sometimes viewed with scepticism, it generally works quite well, and it is backed by the sophisticated machinery of the

renormalization group theory. Scaling is a convenient way of deriving the nonanalytic properties of a system. Classical approaches like perturbation theory and mean-field theory are now known to be invalid in a large number of cases. We could try to work out a polyelectrolyte theory along the lines of ref 41–44, but these methods are bound to fail for the fluctuations in the density are of the same order of magnitude as the average density itself (in semidilute systems).⁴⁵ Renormalization group methods appear to be out of the question too. How does one rigorously take into account the screening of counterions and the change in local flexibility of the chains? If we make certain assumptions like we do here, we need not resort to any renormalization group calculation. In view of Kadanoff's hypothesis of universality,⁶ we may use scaling arguments directly.

Our aim here is to present a picture consistent with existing theoretical knowledge. We expect any refinement to be an exacting task. It seems that solving the statistical mechanics of semidilute polyelectrolyte solutions without salt is still a long way off.

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 (47) Equation 47 should be compared with the counterion pressure $\pi_i \simeq k_B T c_A Q^{-1}$. See also ref 11.
 (48) Two extra critical concentrations can be introduced: (i) c_4 which defines the onset of polymer behavior which a polyelectrolyte inevitably shows at high concentrations; and (ii) $C_G^* \simeq A^{-2/3}$, the overlap concentration defined by De Gennes et al. in ref 11. We have not discussed regions A and E explicitly, but their presence follows from simple arguments.

Imposed Polyelectrolyte Behavior of Poly(*m*-phenyleneisophthalamide) in LiCl/Dimethylacetamide

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ABSTRACT: The dilute solution viscometric behavior of poly(*m*-phenyleneisophthalamide) dissolved in LiCl/dimethylacetamide was studied. Important aspects of this investigation included interactions between dimethylacetamide and LiCl and the capability of poly(*m*-phenyleneisophthalamide) to become a polyion when dissolved in LiCl/dimethylacetamide. Counterion interaction with the polyion and the ability to control the ion concentration gave rise to interesting variations in the hydrodynamic volume of poly(*m*-phenyleneisophthalamide) leading to a maximum in its intrinsic viscosity as a function of LiCl concentration.

A polymer molecule changing its dilute solution viscometric character from typical random coil to polyelectrolyte behavior as salt is added to the solution is contrary to the usual case. Ordinarily a polymer ionizes in a single component solvent and produces a polyelectrolyte. The sodium salt of poly(acrylic acid) dissolved in water is a representative example of the latter case. Such cases show increasing values of η_{sp}/C as C is decreased. However, all of this can be forced to revert to the usual viscometric behavior by the addition of uni-univalent salt.¹

The present study considers the conversion of a polymer to a polyelectrolyte by dissolving it in an ionized solvent. The dilute solution viscometric behavior of poly(*m*-phenyleneisophthalamide) dissolved in the solvents DMA (dimethylacetamide) and DMA/variable LiCl was investigated. To properly discuss the findings of this investigation, some important earlier research on DMA/LiCl interactions and experimental behavior and theory of polyelectrolytes must be recalled.

Amide–LiCl Interactions. Pertinent studies^{2–5} of amide salt solutions reported that in a LiCl/DMF (dimethylformamide) or LiCl/NMA (*N*-methylacetamide) solution it was possible to isolate solid adducts of the salt complexed with the amide. From X-ray and/or titration studies on these adducts, the ratio of LiCl to NMA or DMF was found to be 1 to 4. Viscosity, heats of interaction, and infrared spectroscopy experiments strongly suggest that similar salt–amide complexes are formed in DMA/LiCl solutions. Thus the solvent system LiCl/DMA is significant to the viscometric behavior of polymers manifesting the “polyelectrolyte effect” when dissolved in electrolytic solvents.

Behavior of Polyelectrolytes. Theoretical treatments and experimental techniques dealing with the behavior of polyelectrolytes in dilute solution have been extensively studied and presented in several books.^{6–10} The typical behavior of a linear flexible polyelectrolyte in dilute solution is explained by electrostatic repulsion of the charges along the polyelectrolyte chain causing the macroion to

expand to achieve greater separation of the like charges. Macroion expansion will increase as the polymer concentration is decreased until finally in very dilute solutions the macroion may be fully extended and behave as a rigid rod.^{11–13}

Also the behavior of polyelectrolytes as measured by their $[\eta]$'s in solutions with various levels of added salt is of interest. It has been found experimentally that $[\eta]$ is proportional to $C_s^{-1/2}$ (C_s is the molar concentration of uni-univalent salt, in the present case LiCl) for a number of polyelectrolytes.^{14–16,22} A number of theories exist which deal with the behavior of polyelectrolytes in dilute solutions with added salt.^{1,17–22} Of these theories, those of Fixman, as well as those of Ishihara, predict that $[\eta]$, the intrinsic viscosity, will be proportional to $C_s^{-1/2}$.

Experimental Section

Materials. Two different samples of MPD-I (poly(*m*-phenyleneisophthalamide)) were synthesized in this laboratory using low-temperature solution polycondensation methods. The procedures are in essence those of Morgan and Kwolek and the DuPont group²³ and are described in an earlier paper by our group.²⁴

The solvent system utilized in this investigation was DMA and



LiCl. The DMA was obtained from the Aldrich Chemical Co. and the LiCl from the Mallinckrodt Chemical Co. as reagent grade materials.

Dilute Solution Viscosity. Dilute solution viscosities were determined using an Ubbelohde viscometer at $25 \pm 0.1^\circ\text{C}$ where the flow time of the solvent exceeded 100 s. Data obtained using a number of concentrations were converted to specific and relative viscosities which were converted to intrinsic viscosity $[\eta]$ (when feasible) by extrapolation to infinite dilution. In particular^{25,26}

$$\eta_{sp}/C = [\eta] + k'[\eta]^2C + 0(C^2) \quad (2)$$

and

$$\ln(\eta_{rel}/C) = [\eta] + k''[\eta]^2C + 0(C^2) \quad (3)$$

where k' is the Huggins constant, k'' is the Kraemer constant, and