

Limiting Laws and Counterion Condensation in Polyelectrolyte Solutions

I. Colligative Properties

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Formulas are derived for the osmotic coefficient, the Donnan salt-exclusion factor, and the mobile-ion activity coefficients in a polyelectrolyte solution with or without added sample salt. The formulas, which contain no adjustable parameters, are based on the (theoretical) observation by several workers that counterions will "condense" on the polyion until the charge density on the polyion is reduced below a certain critical value. The uncondensed mobile ions are treated in the Debye-Hückel approximation. In a restricted sense, the formulas are "limiting laws," and this aspect is discussed at length. Detailed comparison with experimental data in the literature is given; agreement of the theory with experiment is usually found to be quantitative.

I. INTRODUCTION

Workers who study the properties of polyelectrolyte solutions have long been at a disadvantage *vis à vis* their colleagues in the field of simple ionic solutions, for the latter have had, for several decades now, the availability of a theory which is generally accepted to be exact—the Debye-Hückel limiting law. Thus, all measurements at finite concentrations can be extrapolated with confidence into very dilute regions and may be referred to as "deviations from the limiting law." All such deviations may then be attributed to effects not taken into account in the derivation of the limiting law (short-range interionic forces, molecular nature of the solvent, etc.), and theories concerning such effects may then be attempted.

On the contrary, no such "reference point" has been available to polyelectrolyte chemists. The high charge density on the polyion implies that many counterions will be attracted to its immediate neighborhood at all concentrations for which measurements can be made. Even at low equivalent concentrations, therefore, the problem is one of concentrated solutions for which a limiting law is not anticipated. For that reason, experimentalists have given equal emphasis to all convenient concentration ranges, while theoreticians have tried to "fit the data" over the entire range of concentration. In practice, the result has been the introduction of adjustable parameters such as effective dielectric constants, mass-action binding constants, polyion size parameters, and effective polyion charge densities (the author has contributed his share), without, however, any really clear idea of what the "ideal" values of such parameters should be, or under what conditions the ideal values would be applicable. For example, while it is obvious that the dielectric constant which appears in the Debye-Hückel limiting law is that which governs the interaction of point charges at large separations, namely, the bulk dielectric constant of the pure solvent, it has not at all been clear that the bulk dielectric constant of water has any relation whatever to the observed

behavior of aqueous polyelectrolyte solutions. Again, for a very dilute solution of sodium chloride, the size and shape of the ions is irrelevant; it is sufficient to specify the valence of each ion. For a solution of sodium polyphosphate, however, it is important to know not only the "valence" of the polyphosphate ion (there are usually of the order of a thousand charged groups on each polyion), but the spatial distribution of the charges on the polyphosphate, that is, the charge *density*. The choice of a charge-density parameter is not obvious on *a priori* grounds.

It is the purpose of this communication to construct a series of plausible and well-motivated assumptions which lead to formulas for several colligative properties of polyelectrolyte solutions. The formulas may be thought of as "limiting laws" in the sense that they are designed specifically for solutions of low equivalent concentration; the number of parameters is thereby reduced to an absolute minimum. Moreover, the numerical values of the parameters are fixed by the assumptions and do not depend in any way on empirical results. Although the formulas are probably not of the same kind of general validity as the Debye-Hückel limiting law, it is hoped that they will serve a similar purpose: to distinguish clearly those effects which dominate at low concentrations from effects which become prominent only with increasing concentration.

II. SPECIFICATION OF THE MODEL

It must first be recognized that, strictly speaking, the Debye-Hückel limiting law is as valid for a polyelectrolyte solution as for any other ionic solution. Thus, in general, if a solution contains σ species of ions with concentrations (number of ions per cc) n_1, \dots, n_σ and valences z_1, \dots, z_σ , then the excess (electrostatic) Helmholtz free energy F^{ex} of the solution at sufficiently low concentrations is given by the limiting law^{1,2}

$$\frac{F^{\text{ex}}}{VkT} = - \left(\frac{4\pi e^2}{\epsilon kT} \sum_{i=1}^{\sigma} n_i z_i^2 \right)^{3/2} (12\pi)^{-1}, \quad (1)$$

¹ R. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, Cambridge, England, 1960).

² J. E. Mayer, *J. Chem. Phys.* **18**, 1426 (1950).

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where V is the volume, e the protonic charge, and ϵ the dielectric constant of the pure solvent. If the σ th species happens to be a polyion bearing a thousand charged groups, one may still assert that, with $|z_\sigma| = 1000$, Eq. (1) will be valid at sufficiently low concentrations. The catch is that for a polyelectrolyte solution, "sufficiently low" turns out to be lower than the minimum concentration required for accurate measurements. For long, densely charged polyelectrolytes (polyphosphate, polyacrylate, DNA, etc.), Debye-Hückel limiting behavior has never been observed at the lowest experimentally feasible concentrations; in particular, colligative properties are invariably found to be independent of molecular weight (i.e., of polyion valence) over the entire concentration range studied.

Such behavior is not unexpected if one considers that interactions of small ions (mobile ions) with the polyelectrolyte chain will be governed primarily by the charged groups on relatively short segments of the chain, contributions from distant groups being screened at the concentrations used. It is thus possible to regard the chain as being infinitely long, at least insofar as interactions of mobile ions with the chain are concerned. Moreover, local chain segments will have a structure determined largely by the electrostatic repulsion of the charged groups and hence will be approximately in a configuration of maximum extension with cylindrical symmetry. Since mobile ions in the vicinity of one segment are screened from charged groups in other segments, the entire (infinitely long) chain may be considered to be in its unique configuration of maximum extension.

It is, furthermore, reasonable to assume that the interactions of the polyion with mobile ions will be primarily dependent on the over-all charge density along the chain, with the discrete nature of the charged groups being a secondary effect ("discrete-charge" effect). Thus, if the contour length of the polyelectrolyte (end-to-end distance in the state of maximum extension) is L , and if the chain bears P charged groups of valence z_p , a uniform linear charge density β is assigned to the chain, given by

$$\beta = z_p e / b, \quad (2)$$

where

$$b = L/P. \quad (3)$$

The above discussion leads naturally to the following model:

(A) *The real polyelectrolyte chain is replaced by an infinite line charge with density β given by Eqs. (2) and (3).*

It should be emphasized that β may not be treated as an adjustable parameter, for the only value consistent with the model of a line charge is that given by Eqs. (2) and (3) and is calculable from the known structure of the particular polyelectrolyte under study. Cylindrically

symmetric models have been previously used by many authors,³⁻¹² usually with the additional specification of a distance of closest approach (formulated as a cylinder of finite radius with uniform surface charge density). Since this communication deals only with limiting laws, such specification will not be necessary.

When a simple salt, e.g., sodium chloride, is present in excess over the equivalent polyelectrolyte concentration, one may rigorously neglect electrostatic interactions between polyions in comparison to interactions between a polyion and mobile ions in its vicinity; such, however, is not the case in salt-free solutions.⁹ Nevertheless, it has been assumed above that local segments of a polyion are screened from other segments on the same polyion, and it is only consistent to assume that segments on different polyions are likewise screened from each other. Thus,

(B) *interactions between two or more polyions are neglected regardless of the ratio of polyelectrolyte concentration to that of added simple salt.*

In common with nearly all other theories of ionic solutions, the solvent will be regarded as a continuum with a uniform dielectric constant ϵ . It is stated at the outset that

(C) *the dielectric constant ϵ is taken as that of the pure bulk solvent.*

In the context of the present article, justification of this assumption is primarily that it will lead to results which agree with experiment. It is, in fact, possible to understand on physical grounds why the local structure of the solvent in the immediate vicinity of the polyion chain does not affect colligative properties at low equivalent concentrations; an approach other than the present one is needed, however, and will be the subject of a future publication in this series.

The next two assumptions are not familiar and require detailed discussion. Onsager¹³ has observed that the statistical-mechanical phase integral for an infinite line-charge model diverges for all values of β greater than a critical value. This phenomenon is easily verified. If ρ denotes distance from the line charge, then the electrostatic energy of a mobile ion (considered as a

³ T. Alfrey, P. W. Berg, and H. Morawetz, *J. Polymer Sci.* **7**, 543 (1951).

⁴ R. M. Fuoss, A. Katchalsky, and S. Lifson, *Proc. Natl. Acad. Sci. U.S.A.* **37**, 579 (1951).

⁵ S. Lifson and A. Katchalsky, *J. Polymer Sci.* **13**, 43 (1954).

⁶ F. Oosawa, *J. Polymer Sci.* **23**, 421 (1957).

⁷ U. P. Strauss, *J. Am. Chem. Soc.* **80**, 6498 (1958).

⁸ L. Kotin and M. Nagasawa, *J. Chem. Phys.* **36**, 873 (1962).

⁹ G. S. Manning and B. H. Zimm, *J. Chem. Phys.* **43**, 4250 (1965).

¹⁰ A. Katchalsky, Z. Alexandrowicz, and O. Kedem, in *Chemical Physics of Ionic Solutions*, B. E. Conway and R. G. Barradas, Eds. (John Wiley & Sons, Inc., New York, 1966), p. 295.

¹¹ L. M. Gross and U. P. Strauss, in *Chemical Physics of Ionic Solutions*, B. E. Conway and R. G. Barradas, Eds. (John Wiley & Sons, Inc., New York, 1966), p. 347.

¹² A. D. MacGillivray, *J. Chem. Phys.* **45**, 2184 (1966).

¹³ L. Onsager (informal discussion).

point charge) of valence z_i for sufficiently small values of ρ , say for $\rho \leq \rho_0$, is given by the unscreened Coulomb interaction,

$$u_{ip} = -z_i e (2\beta/\epsilon) \ln \rho, \quad \rho \leq \rho_0. \quad (4)$$

The contribution $A_i(\rho_0)$ to the phase integral of the region in which mobile ion i is within a distance ρ_0 of the line charge, while all other mobile ions are at a distance greater than ρ_0 , thereby contributing a finite factor $f(\rho_0)$, is given by

$$\begin{aligned} A_i(\rho_0) &= f(\rho_0) \int_0^{\rho_0} \exp\left(-\frac{u_{ip}(\rho)}{kT}\right) 2\pi\rho d\rho \\ &= 2\pi f(\rho_0) \int_0^{\rho_0} \rho^{(1+2z_i z_p \xi)} d\rho, \end{aligned} \quad (5)$$

where

$$\xi = e^2/\epsilon kTb, \quad (6)$$

Eq. (2) for β having been used. If ion i is a counterion, so that $z_i z_p < 0$, the integral in Eq. (5) diverges at the lower limit for all ξ such that

$$\xi \geq |z_i z_p|^{-1}. \quad (7)$$

Attention will be restricted in the following to monovalent charged groups and mobile ions, so the condition (7) becomes

$$\xi \geq 1. \quad (8)$$

For water at 25°C ($\epsilon=78.5$), the critical value $\xi=1$ corresponds to the charge spacing $b=7.135$ Å. It will be recognized that the quantity $(e^2/\epsilon kT)$ is the "Bjerrum length" of the classical theory of simple electrolyte solutions¹; the critical charge spacing is therefore equal to the Bjerrum length.

The physical interpretation of the divergence of the phase integral for values of ξ greater than unity is that systems characterized by such values are unstable: sufficiently many counterions will "condense" on the line charge to reduce ξ to a value just less than one. Although the argument presented is valid at arbitrary concentrations for an infinitely thin line charge, it will be shown in a future article that for a more realistic model with a finite distance of closest approach, the instability condition (8) is valid only in the limit of zero concentration; the instability is a "limiting law." The assumption, then, is as follows:

(D) *For dilute solutions, sufficiently many counterions will "condense" on the polyanion to lower the charge-density parameter ξ to the value one.*

The critical nature of the point $\xi=1$ has in fact been noted previously by a number of authors, but not from as fundamental a point of view as Onsager's. From their detailed analyses of the Poisson-Boltzmann equation as applied to various problems involving rodlike

charges, Imai, Onishi, and Oosawa¹⁴ deduced the special significance of the condition $\xi=1$ and, indeed, the terminology "counterion condensation" is to be attributed to them. (I have chosen "condensation" over "binding" primarily because the latter term means so many different things to so many different people.) Jackson and Coriell,¹⁵ while studying the Brownian motion of a counterion in the neighborhood of a line charge, found the onset of "trapped trajectories" at $\xi=1$ and speculated about their relation to the concept of "ion association." As long ago as 1951, Fuoss, Katchalsky, and Lifson⁴ noted that their exact solution of the cylindrically symmetric Poisson-Boltzmann equation in salt-free solutions exhibited qualitatively different behavior for small values of ξ than for large values; although, being interested in the case of a cylinder with finite radius and finite concentrations, they did not emphasize the transition point $\xi=1$. Gross and Strauss¹¹ and MacGillivray¹² also noticed the importance of the condition $\xi=1$; their contribution will be discussed in the context of the next assumption.

The uncondensed mobile ions are still subject to electrostatic interactions with the line charge since the charge density of the line after condensation is not zero: if the value of ξ before condensation is greater than one, the value after condensation is equal to one; if it is less than one, there is no condensation and all mobile ions are subject to the full charge density of the line. It is now assumed that:

(E) *The uncondensed mobile ions may be treated in the Debye-Hückel approximation.*

In support of this assumption it may be noted that MacGillivray¹² has demonstrated, from both an analytical and numerical study of the cylindrically symmetric Poisson-Boltzmann equation, that the solution of the linearized equation is a good approximation to the solution of the complete equation for all values of $\xi < 1$. His result is by no means trivial since for dilute solutions, $e\psi/kT \gg 1$ at the distance of closest approach, where ψ is the electrostatic potential. Second, from a purely numerical solution of the Poisson-Boltzmann equation Gross and Strauss¹¹ derived the following expressions for Γ , the Donnan salt-exclusion factor, cf. Eq. (30):

$$\lim_{n_s \rightarrow 0} \Gamma = \frac{1}{2}(1 - \frac{1}{2}\xi), \quad \xi < 1 \quad (9a)$$

$$= (4\xi)^{-1}, \quad \xi > 1. \quad (9b)$$

The limit refers to the concentration of salt in the external compartment. As will be seen in Sec. III, the expression (9a) is precisely that obtained from the Debye-Hückel approximation. Finally, Lifson and

¹⁴ N. Imai and T. Onishi, J. Chem. Phys. **30**, 1115 (1959). T. Onishi, N. Imai and F. Oosawa, J. Phys. Soc. Japan **15**, 896 (1960); N. Imai, *ibid.* **16**, 746 (1961).

¹⁵ J. L. Jackson and S. R. Coriell, J. Chem. Phys. **40**, 1460 (1964).

Katchalsky⁵ calculated the osmotic coefficient ϕ_p of a salt-free polyelectrolyte solution from an exact analytical solution of the appropriate Poisson-Boltzmann equation. Their result, when applied to the limit as n_e , the equivalent polyelectrolyte concentration, tends to zero, is

$$\lim_{n_e \rightarrow 0} \phi_p = 1 - \frac{1}{2}\xi, \quad \xi < 1 \quad (10a)$$

$$= (2\xi)^{-1}, \quad \xi > 1. \quad (10b)$$

Again, it will be shown in Sec. III that (10a), the expression for $\xi < 1$, is the same as that given by the Debye-Hückel approximation.

The analogy of the last two assumptions to the Bjerrum theory of simple electrolytes¹ is striking. All deviations from Debye-Hückel behavior are attributed to counterion condensation (ion pairs for simple electrolytes). Bjerrum calculated the extent of pairing from the partition function of an ion pair; the extent of condensation has also been determined here from the partition function (phase integral). Moreover, the Bjerrum length ($e^2/\epsilon kT$) turns out to be central to both theories.

III. THE CASE $\xi < 1$

According to Assumption (E) of the preceding section, the case $\xi < 1$ may be treated in the Debye-Hückel approximation. The potential $\psi(\rho)$ at a distance ρ from the line charge (taken along the z axis) is thus given by a superposition of screened Coulomb potentials from infinitesimal segments of length dz :

$$\begin{aligned} \psi(\rho) &= \frac{\beta}{\epsilon} \int_{-\infty}^{\infty} \left(\frac{\exp[-\kappa(\rho^2 + z^2)^{1/2}]}{(\rho^2 + z^2)^{1/2}} \right) dz \\ &= \frac{2\beta}{\epsilon} \int_1^{\infty} \frac{\exp(-\kappa \rho t)}{(t^2 - 1)^{1/2}} dt \\ &= (2\beta/\epsilon) K_0(\kappa\rho), \end{aligned} \quad (11)$$

where the integral in the second line has been noted to be a representation of $K_0(\kappa\rho)$, the zeroth-order modified Bessel function of the second kind. If two species 1 and 2 of monovalent mobile ions are present, the Debye screening parameter κ is given by

$$\kappa^2 = \lambda(n_1 + n_2), \quad (12)$$

with

$$\lambda = 4\pi e^2/\epsilon kT. \quad (13)$$

The function $K_0(\kappa\rho)$ has the asymptotic behavior

$$K_0(\kappa\rho) \sim -\ln \kappa\rho, \quad \kappa\rho \rightarrow 0, \quad (14)$$

so that, when ρ is allowed to tend to zero in Eq. (11), the potential $\psi'(0)$ at the position of the line charge due to the mobile ions is seen to be

$$\psi'(0) = -(2\beta/\epsilon) \ln \kappa; \quad (15)$$

the term proportional to $\ln \rho$ is the potential due to the line charge itself. The excess free energy $f^{\text{ex}} dz$ associated

with the segment dz of the line charge, that is, the free energy attributable to interactions between the segment and mobile ions, may be obtained by "charging" the segment up to the charge βdz starting from zero charge. This procedure amounts to the integration of Eq. (15) from $\beta=0$ to the final value β :

$$f^{\text{ex}} dz = -(\beta^2/\epsilon) \ln \kappa dz. \quad (16)$$

The total excess free energy F^{ex} of the solution of volume V is set equal to

$$N_p \int_{-\infty}^{\infty} f^{\text{ex}} dz,$$

where N_p is the number of polyions in the solution so that, when Eq. (2) is used for β (with $|z_p| = 1$),

$$F^{\text{ex}}/V kT = -\xi n_e \ln \kappa, \quad \xi < 1, \quad (17)$$

where the definition (6) of ξ has been used, and

$$b^{-1} \int_{-\infty}^{\infty} dz$$

has been given the obvious interpretation as the number P of charged groups on each polyion; the equivalent concentration n_e is then

$$n_e = P N_p / V. \quad (18)$$

Equation (17) is the desired Debye-Hückel approximation to the excess free energy for $\xi < 1$. The problem of units raised by the appearance of the factor $\ln \kappa$ is only apparent, for all measurable quantities to be calculated from Eq. (17) will have proper units. Actually only part of the excess free energy is given by Eq. (17) since the charging procedure was not applied to the charge on the mobile ions. The contribution of mobile ions may be shown⁹ to be of higher order in κ and is neglected here.

Having obtained an expression for the excess Helmholtz free energy, one may easily derive deviations from ideality of various colligative properties. Thus, with the derivatives

$$\partial \kappa / \partial n_i = \lambda / 2\kappa, \quad i = 1, 2, \quad (19)$$

the activity coefficients of the mobile ions follow as

$$\begin{aligned} \ln \gamma_i &= \left(\frac{\partial (F^{\text{ex}}/V kT)}{\partial n_i} \right)_{T, V, n_{j \neq i}} \\ &= -\frac{1}{2} \xi \lambda n_e \kappa^{-2}, \quad i = 1, 2; \xi < 1. \end{aligned} \quad (20)$$

It is useful to write this equation in another form. If Species 1 is the counterion, then

$$n_1 = n_e + n_s, \quad (21)$$

where n_s is the concentration of uni-univalent salt added to the polyelectrolyte solution; while for Species 2, the co-ion

$$n_2 = n_s. \quad (22)$$

With the use of Eq. (12) and the quantity

$$X = n_e/n_s, \quad (23)$$

Eq. (20) becomes

$$\ln \gamma_i = -\frac{1}{2}\xi X(X+2)^{-1}, \quad i=1, 2; \xi < 1. \quad (24)$$

The same formula holds for the mean activity coefficient γ_{\pm} of the mobile ions:

$$\begin{aligned} \ln \gamma_{\pm} &= \frac{1}{2}(\ln \gamma_1 + \ln \gamma_2) \\ &= -\frac{1}{2}\xi X(X+2)^{-1}, \quad \xi < 1. \end{aligned} \quad (25)$$

The osmotic coefficient ϕ is easily calculated from Eq. (17) with the help of the derivative ($n_i = N_i/V$, where N_i is the number of ions of species i),

$$(\partial \kappa / \partial V)_{N_i} = -\kappa / 2V. \quad (26)$$

Indeed, since ϕ is defined in terms of the excess part of the osmotic pressure π^{ex} ,

$$kT(\phi - 1)(n_1 + n_2) = \pi^{\text{ex}} = -(\partial F^{\text{ex}} / \partial V)_{T, N_p, N_1, N_2}, \quad (27)$$

one gets,

$$\phi = 1 - \frac{1}{2}\xi X(X+2)^{-1}. \quad (28)$$

In Eq. (27), the contribution of the concentration n_p of the polyions has been neglected with respect to n_e , the minimum value of $(n_1 + n_2)$. For the salt-free case, $n_s = 0$ and $X \rightarrow \infty$, while ϕ is denoted by ϕ_p ; thus,

$$\phi_p = 1 - \frac{1}{2}\xi, \quad \xi < 1, \quad (29)$$

in agreement with the Lifson-Katchalsky result, Eq. (10a).

Consider now a Donnan equilibrium in which the external compartment has the fixed salt concentration n_s' . The internal compartment, which contains the polyelectrolyte solution, will have a lower salt concentration n_s . The Donnan salt-exclusion factor Γ is defined by

$$\Gamma = \lim_{n_e \rightarrow 0} (n_s' - n_s) / n_e. \quad (30)$$

It may be shown that¹¹

$$\begin{aligned} \Gamma &= \left[\frac{1}{2} + n_s' (\partial \ln \gamma_{\pm} / \partial n_e)_{n_e \rightarrow 0} \right] \left[1 + n_s' (\partial \ln \gamma_{\pm}' / \partial n_s') \right]^{-1} \\ &\approx \frac{1}{2} + n_s' (\partial \ln \gamma_{\pm} / \partial n_e)_{n_e \rightarrow 0}, \end{aligned} \quad (31)$$

where the derivative of $\ln \gamma_{\pm}$, the mean activity coefficient of the mobile ions in the internal compartment, is to be evaluated in the limit of zero polyion concentration, i.e., in the limit as n_s tends to n_s' ; the approximation introduced in the second line becomes exact as n_s' tends to zero. Note that the ideal value ($\gamma_{\pm} = \gamma_{\pm}' = 1$) of Γ is $\frac{1}{2}$. It follows from Eqs. (25) and (31) that

$$\Gamma = \frac{1}{2}(1 - \frac{1}{2}\xi), \quad \xi < 1, \quad (32)$$

in agreement with the result of Gross and Strauss, Eq. (9a) [their Eq. (26)].

IV. THE CASE $\xi > 1$

In this section one must distinguish between "real" and "effective" values. The symbol ξ refers to the real value, that is, the value calculated from Eq. (6) and a structural model of the polyion under study. According to Assumption (D) of Sec. II, however, when the real value of ξ is greater than unity, its *effective* value will be equal to one since condensed counterions will neutralize the fraction $(1 - \xi^{-1})$ of the polyion charge. Similarly, while the real (stoichiometric) concentration of counterions is $(n_e + n_s)$, the effective value (uncondensed counterions) is $(\xi^{-1}n_e + n_s)$. The stoichiometric and effective concentrations of the co-ion have, of course, the same value n_s .

The simplest example is the salt-exclusion factor Γ . It follows from Eq. (30) that, to terms of order n_e ,

$$n_s' - n_s = n_e \Gamma. \quad (33)$$

But because the effective equivalent polyelectrolyte concentration is $\xi^{-1}n_e$, it is also the case that

$$n_s' - n_s = \xi^{-1}n_e \Gamma(1), \quad (34)$$

where $\Gamma(1)$ is the salt-exclusion factor for a polyelectrolyte with $\xi = 1$. According to Assumption (E) of Sec. II, $\Gamma(1)$ may be obtained simply by setting $\xi = 1$ in the Debye-Hückel approximation to Γ given by Eq. (32),

$$\Gamma(1) = \frac{1}{4}. \quad (35)$$

Identification of the right-hand sides of Eqs. (33) and (34), together with Eq. (35), yields the desired result:

$$\Gamma = (4\xi)^{-1}, \quad \xi > 1. \quad (36)$$

This expression agrees with Eq. (9b), found by Gross and Strauss from a numerical solution of the Poisson-Boltzmann equation.

The derivation of the osmotic coefficient ϕ for values of $\xi > 1$ is similar. The osmotic pressure π of the solution is given by

$$\pi / kT = \phi(n_1 + n_2) = \phi(n_e + 2n_s). \quad (37)$$

On the other hand, since the effective concentration of mobile ions is $(\xi^{-1}n_e + 2n_s)$ and the effective charge density of the polyion corresponds to $\xi = 1$,

$$\pi / kT = \phi(1, \xi^{-1}n_e)(\xi^{-1}n_e + 2n_s), \quad (38)$$

where $\phi(1, \xi^{-1}n_e)$ is the osmotic coefficient of a solution whose polyelectrolyte species has charge density $\xi = 1$ and equivalent concentration $\xi^{-1}n_e$, and whose concentration of added salt is the same value n_s . The Debye-Hückel approximation to this quantity is obtained from Eq. (28) with $\xi = 1$ and with $X = n_e/n_s$ replaced by $\xi^{-1}X$:

$$\phi(1, \xi^{-1}n_e) = 1 - \frac{1}{2}\xi^{-1}X(\xi^{-1}X + 2)^{-1}. \quad (39)$$

Combination of Eqs. (37)–(39) yields the simple result

$$\phi = (\frac{1}{2}\xi^{-1}X + 2) / (X + 2), \quad \xi > 1. \quad (40)$$

In salt-free solutions ($\phi \equiv \phi_p$, $X \rightarrow \infty$), Eq. (40) reduces to

$$\phi_p = (2\xi)^{-1}, \quad \xi > 1, \quad (41)$$

in agreement with the Lifson-Katchalsky result, Eq. (10b).

Activity coefficients are also easily obtained. The stoichiometric activity of the counterion a_1 is given by

$$a_1 = \gamma_1 n_1 = \gamma_1 (n_e + n_s). \quad (42)$$

Another expression for a_1 in terms of "effective" quantities is

$$a_1 = \gamma_1(1, \xi^{-1}n_e)(\xi^{-1}n_e + n_s), \quad (43)$$

where $\gamma_1(1, \xi^{-1}n_e)$ has a meaning analogous to the corresponding osmotic coefficient in Eq. (38) and is obtained from Eq. (24),

$$\gamma_1(1, \xi^{-1}n_e) = \exp[-\frac{1}{2}\xi^{-1}X/(\xi^{-1}X+2)]. \quad (44)$$

It follows that

$$\gamma_1 = (\xi^{-1}X+1)(X+1)^{-1} \exp[-\frac{1}{2}\xi^{-1}X/(\xi^{-1}X+2)], \quad \xi > 1. \quad (45)$$

The activity coefficient of the co-ion is trivially obtained as

$$\gamma_2 = \gamma_2(1; \xi^{-1}n_e) \quad (46)$$

or

$$\gamma_2 = \exp[-\frac{1}{2}\xi^{-1}X/(\xi^{-1}X+2)], \quad \xi > 1. \quad (47)$$

For the square of the mean activity coefficient of the mobile ions,

$$\gamma_{\pm}^2 = \gamma_1 \gamma_2 = (\xi^{-1}X+1)(X+1)^{-1} \times \exp[-\xi^{-1}X/(\xi^{-1}X+2)], \quad \xi > 1. \quad (48)$$

As a check, it may be verified that when Γ is calculated directly from Eqs. (31) and (48), the result (36) is recovered.

V. ADDITIVITY RULES

A number of interesting correlations may be found among the formulas of the two preceding sections. For example, comparison of Eq. (29) with Eq. (32), and Eq. (36) with Eq. (41) indicates that for all values of ξ ,

$$\Gamma = \frac{1}{2}\phi_p, \quad (49)$$

a formula which has been observed to agree well with experimental data for dilute solutions.¹⁶ Moreover, Eqs. (28), (29), (40), and (41) show that, again for all ξ ,

$$\phi(n_e + 2n_s) = \phi_p n_e + 2n_s. \quad (50)$$

Equation (50) is a well-known formulation of the empirical "additivity rule" for the osmotic coefficient in dilute solutions.¹⁰

Equations (49) and (50) have been interpreted as meaning that the fraction $(1-\phi_p)$ of the counterions

from the polyelectrolyte salt is "bound" to the polyion, while the remaining fraction is "free," that is, does not interact with the polyion; mobile ions from the added simple salt are also assumed not to interact with the polyion. Thus, Eq. (49) would merely say that Γ is given by its ideal value with an effective equivalent polyion concentration $\phi_p n_e$; Eq. (50) would mean that the osmotic pressure is given by van't Hoff's law as applied only to the free concentration of mobile ions.

The present theory offers a different interpretation of Eqs. (49) and (50). Since it is clear that only condensed counterions should be classified as "bound," there are no bound counterions at all when $\xi < 1$; Eqs. (49) and (50) then follow entirely from the Debye-Hückel (diffuse ion atmosphere) treatment of all the mobile ions. When $\xi > 1$, the fraction of condensed, or bound, counterions is $(1-\xi^{-1})$, whereas $\phi_p = \frac{1}{2}\xi^{-1}$ [see Eq. (41)]; therefore, $(1-\phi_p)$ is not the fraction of bound counterions but rather reflects a combination of bound counterions and the effect of Debye-Hückel interactions on the uncondensed counterions.

The relation between the activity coefficients and the osmotic coefficient is also of interest. If the counterion activity coefficient in salt-free solutions is denoted by γ_1^p , Eqs. (24) and (45) yield the results

$$\ln \gamma_1^p = -\frac{1}{2}\xi, \quad \xi < 1, \quad (51a)$$

$$\gamma_1^p = \xi^{-1}e^{-1/2}, \quad \xi > 1. \quad (51b)$$

On comparison of these expressions with Eqs. (29) and (41), the relations

$$\phi_p = 1 + \ln \gamma_1^p, \quad \xi < 1 \quad (52a)$$

$$\gamma_1^p / \phi_p = 2e^{-1/2} \approx 1.21, \quad \xi > 1 \quad (52b)$$

are obtained. These formulas differ from the conclusion of Katchalsky, Alexandrowicz, and Kedem¹⁰ that $\gamma_1^p = \phi_p$.

For solutions which contain an added simple salt, a relation between the osmotic coefficient and the mean activity coefficient of the mobile ions is given by Eqs. (25) and (28):

$$\phi = 1 + \ln \gamma_{\pm}, \quad \xi < 1. \quad (53)$$

Equation (53) does not hold in general when $\xi > 1$, but imposition of the condition of excess salt, $X \ll 1$, on Eqs. (40) and (48) yields

$$\phi = 1 + \ln \gamma_{\pm}, \quad (\xi > 1, X \ll 1), \quad (54)$$

a formula which agrees well with experimental data.⁹

Finally, if Eq. (50) is solved for ϕ subject to the condition $X \ll 1$ ($n_e \ll n_s$) and the result substituted into Eqs. (53) and (54), the "additivity rule" for the mean activity coefficient is obtained (for either $\xi < 1$ or $\xi > 1$):

$$\gamma_{\pm}^2(n_e + n_s) = \phi_p n_e + n_s, \quad (n_e/n_s) \ll 1. \quad (55)$$

(If both sides of this equation are multiplied by n_s ,

¹⁶ Z. Alexandrowicz and A. Katchalsky, J. Polymer Sci. **A1**, 3231 (1963).

TABLE I. Comparison of theoretical with experimental values of Γ .

System	Reference	ξ^a	Γ_{exptl}^b	$\Gamma_{\text{theoret}}^c$
NaPVS; NaCl	18	1.85	0.10	0.14
KPP; KBr	19	2.85	0.08	0.09
KDNA; KBr	20	4.20	0.09	0.06
NaPA; NaBr ($\alpha=0.8$)	16	2.28	0.11	0.11
NaPA; NaBr ($\alpha=0.3$)	16	0.86	0.24	0.29
NaPA; NaBr ($\alpha=0.1$)	16	0.29	0.38	0.43

^a Calculated from Eqs. (3) and (6).^b In each case, these values correspond to the lowest salt concentration used in the measurements.^c Calculated from Eq. (32) or Eq. (36).

the interpretation in terms of "bound" and "free" ions becomes clear: the lhs is the product of the activities of counter- and co-ions; the rhs would be the product of the respective "free" concentrations.) It is to be noted that ϕ_p , not γ_1^p , appears in Eq. (55); empirical formulations of the additivity rules have sometimes used the assumption that $\phi_p = \gamma_1^p$, which is not true for the present theory. It is also significant that Eq. (55) is restricted by the condition of excess salt, while Eq. (50) holds for any value of the ratio (n_e/n_s); previous discussions of the additivity rules treat both formulas on the same footing.

Incidentally, the additivity rule for the counterion alone does *not* hold here. Thus, from Eq. (45),

$$\gamma_1(n_e + n_s) = (3/4\xi)n_e + n_s \\ = (3/2)\phi_p n_e + n_s, \quad [\xi > 1, (n_e/n_s) \ll 1]; \quad (56)$$

whereas the additivity rule replaces the factor 3/2 with unity. For the co-ion, from Eq. (47),

$$\gamma_2 n_s = n_s - \frac{1}{4}\xi^{-1} n_e \\ = n_s - \frac{1}{2}\phi_p n_e, \quad [\xi > 1, (n_e/n_s) \ll 1]; \quad (57)$$

the additivity rule (all co-ions are "free") would read $\gamma_2 n_s = n_s$, i.e., $\gamma_2 = 1$. It is of interest in this connection that Lyons and Kotin have recently concluded on experimental grounds that the additivity rule for the counterion is not valid.¹⁷

VI. COMPARISON WITH EXPERIMENT

This section will be devoted to a fairly comprehensive survey of the available data and their treatment by means of the formulas developed in the preceding sections. Numerical values of ξ are all calculated from Eqs. (3) and (6), $\xi = 7.135b^{-1}$ (25°C), where, for example, $b = 2.5$ Å for polyphosphate or fully charged vinylic polyelectrolytes. If the fraction α of vinylic monomeric groups is charged, $b = 2.5\alpha^{-1}$. For native DNA, $b = 1.7$ Å.

¹⁷ J. W. Lyons and L. Kotin, J. Am. Chem. Soc. **87**, 1670 (1965).

The following abbreviations are used: PA (polyacrylate); PMA (polymethacrylate); PP (polyphosphate); PVS (polyvinyl sulfate); PSS (polystyrene sulfonate); PES (polyethylene sulfonate); DNA (deoxyribonucleic acid).

Table I has been constructed for the Donnan salt-exclusion factor. The first thing to note is that the theoretical values of Γ , calculated from Eq. (32) or Eq. (36) according to whether ξ is less than or greater than unity, are all in good agreement with the measured values.^{16,18-20} Since the theory gives the "limiting" values of Γ as the salt concentration tends to zero, the observed value of Γ listed in Table I is in each case that for the lowest salt concentration used. Note also that for the last three systems, which differ only in the values of ξ , the observable trend is for Γ to increase toward its ideal value of 0.5 with decreasing charge density, and that the theoretical values follow this trend fairly well.

In Fig. 1 an attempt is made to illustrate the "limiting-law" concept for polyelectrolyte solutions. The data for the KDNA system²⁰ (open circles) and for the KPP system¹⁹ (filled circles) are plotted in Fig. 1(a) as a function of external salt concentration. The theory [Eq. (36)] predicts that with decreasing concentration the open circles should converge to the intercept of the lower dashed line, while the filled circles should converge to the (more or less equal) intercept of the upper dashed line. The data are inconclusive in that regard, but the trend for the two sets of points to become more alike as n_s' decreases is obvious. In Fig. 1(b), both sets of points are for polyphosphate, but the open circles represent values when tetramethylammonium (TMA⁺) is used as the counterion; the salt is TMABr. The

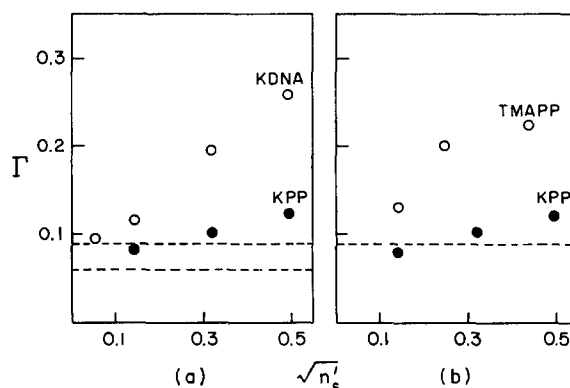


FIG. 1. In (a), open circles are data for system KDNA-KBr (Ref. 20); filled circles for KPP-KBr (Ref. 19). Dashed lines are respective values of Γ_{theoret} ; see Table I. In (b), open circles are data for TMAPP-TMA⁺; filled circles are same data as in (a). Dashed line is value of Γ_{theoret} for PP ($\xi = 2.85$). n_s' (equivalents/liter) is salt concentration in external compartment.

¹⁸ M. Nagasawa, A. Takahashi, M. Izumi, and I. Kagawa, J. Polymer Sci. **38**, 213 (1959).¹⁹ U. P. Strauss and P. Ander, J. Am. Chem. Soc. **80**, 6494 (1958).²⁰ U. P. Strauss, C. Helfgott, and H. Pink, J. Phys. Chem. **71**, 2550 (1967).

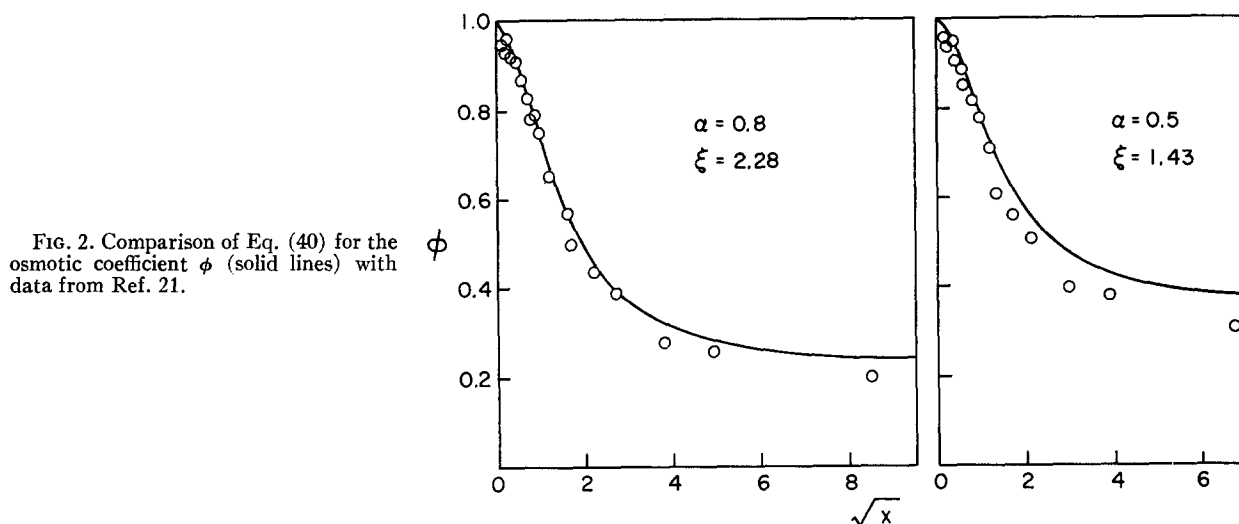


FIG. 2. Comparison of Eq. (40) for the osmotic coefficient ϕ (solid lines) with data from Ref. 21.

closed circles are the same KPP data as in Fig. 1(a). The theory predicts that both sets of points will converge to the intercept of the dashed line. Again, the data are inconclusive, but it looks as though the TMA+ and K+ points could be converging to the same value. The theory predicts only the intercept; Fig. 1 is not meant to imply that the slope should be zero.

Alexandrowicz²¹ has published extensive data for the osmotic coefficient ϕ and the mean activity coefficient γ_{\pm} of the mobile ions. The system is NaPMA with various degrees of neutralization α and with added NaBr. In Fig. 2, the data for ϕ are plotted as a function of $X^{1/2}$ and compared with the theoretical expression

given by Eq. (40). The points cover a range of values of the total mobile ion concentration n ,

$$n = n_e + 2n_s, \quad (58)$$

varying from $1.4 \times 10^{-3} N$ to $0.17 N$. Data for γ_{\pm} (Alexandrowicz's quantity f_s is equal to γ_{\pm}^2) are shown in Fig. 3 for a similar concentration range of n ; the theoretical curve is found from Eq. (48).

If Eqs. (40) and (48) are to be interpreted as limiting laws, then they give the limiting value of ϕ and γ_{\pm} , respectively, for a fixed value of X as n tends to zero. Data over a wide concentration range for a fixed value of X are not available at present, but the inset in Fig. 3 is intended to show the possibilities of such a point of view. The lower point is the value of γ_{\pm} measured when $n = 0.17 N$; the upper point is that measured at $n = 0.006 N$. In both cases, $X \approx 1$. The theory is in excellent agreement with the value of γ_{\pm} in the more dilute solution.

In Fig. 4, curves computed from Eqs. (45) and (47) are compared with measured values of the single-mobile-ion activity coefficients.^{17,22} Both sets of data were taken for the system NaPVS with added NaCl, although ξ is somewhat higher for γ_1 , the sodium activity coefficient,¹⁷ than for γ_2 , the chloride activity coefficient.²² The value of n ranges from $1.9 \times 10^{-3} N$ – $3.2 \times 10^{-2} N$ for γ_1 and from $3 \times 10^{-3} N$ – $4.5 \times 10^{-2} N$ for γ_2 . Nagasawa, Izumi, and Kagawa²² also measured γ_{Na^+} for their system with the use of a sodium amalgam electrode; their values (not included in Fig. 4) are lower than those predicted by Eq. (45). Lyons and Kotin¹⁷ used a cation-exchange resin for their measurements of γ_{Na^+} ; Nagasawa *et al.* used a AgCl electrode for γ_{Cl^-} .

Lyons and Kotin¹⁷ also report counterion activity coefficients for NaPSS and NaPP, both with added NaCl. These data (along with some points from Fig.

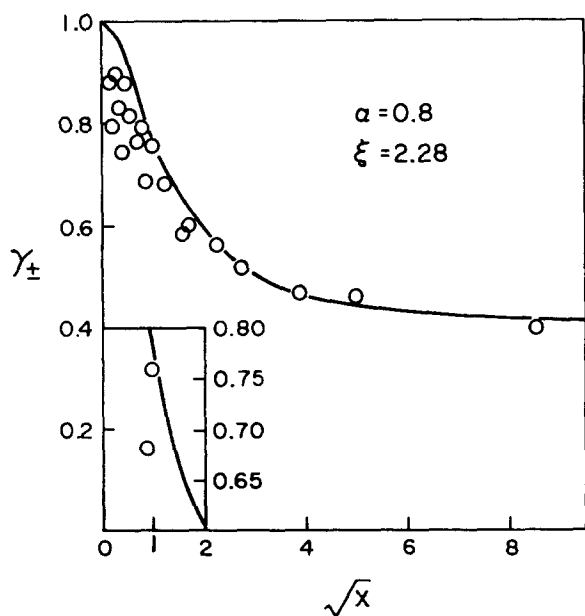


FIG. 3. Comparison of Eq. (48) for the mean activity coefficient γ_{\pm} (solid line) with data from Ref. 21.

²¹ Z. Alexandrowicz, J. Polymer Sci. **43**, 337 (1960).

²² M. Nagasawa, M. Izumi, I. Kagawa, J. Polymer Sci. **37**, 375 (1959).

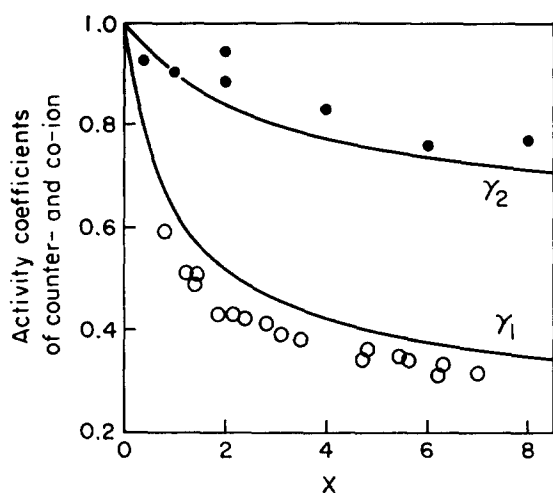


FIG. 4. Comparison of Eq. (45) for the counterion activity coefficient γ_1 (lower solid line; $\xi=2.36$) and Eq. (47) for the co-ion activity coefficient γ_2 (upper solid line; $\xi=1.85$) with data from Refs. 17 and 22, respectively.

4) are shown in Table II. Note in particular that, in accordance with the theory, the measured values of γ_1 are the same for fixed values of X .

Data are plentiful for the counterion activity coefficient γ_1^p in salt-free solutions.^{17,23-27} With very few

TABLE II. Experimental and theoretical values of γ_1 .

$n_e \times 10^3 (N)$	$n_s \times 10^3 (N)$	X	γ_1 (exptl) ^a	γ_1 [Eq. (45)]
(NaPSS; NaCl), $\xi=2.34$				
0.293	0.107	2.74	0.47	0.49
9.11	3.34	2.73	0.47	0.49
1.97	0.673	2.93	0.45	0.47
(NaPP; NaCl), $\xi=2.85$				
0.310	0.099	3.13	0.46	0.42
0.613	0.196	3.13	0.47	0.42
1.25	0.398	3.14	0.46	0.42
2.48	0.794	3.12	0.46	0.42
4.93	1.38	3.57	0.40	0.41
9.75	1.53	6.37	0.42	0.34
(NaPVS; NaCl), $\xi=2.37$				
3.04	2.20	1.38	0.51	0.59
7.34	5.32	1.38	0.49	0.59
45.7	33.7	1.36	0.48	0.59

^a Taken from Ref. 17.

²³ W. Kern, Makromol. Chemie 2, 279 (1948).

²⁴ M. Nagasawa and I. Kagawa, J. Polymer Sci. 25, 61 (1957).

²⁵ A. M. Liquori, S. Ascoli, C. Bottré, V. Crescenzi, and A. Mele, J. Polymer Sci. 40, 169 (1959).

²⁶ T. Okubo, Y. Nishizaki, and N. Ise, J. Phys. Chem. 69, 3690 (1965).

²⁷ L. Costantino, V. Crescenzi, F. Quadrioglio, and V. Vi-tagliano, J. Polymer Sci. A5, 771 (1967).

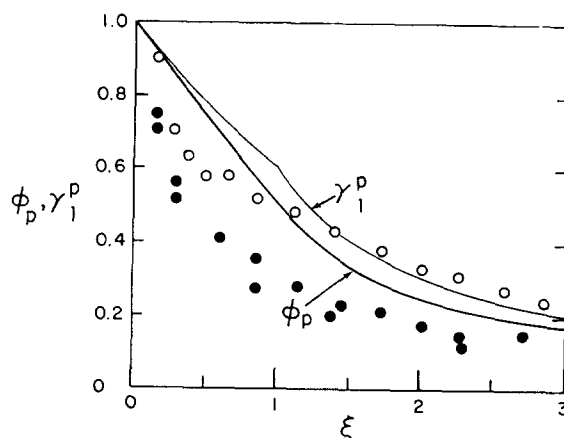


FIG. 5. Comparison of Eqs. (51a) and (51b) for the counterion activity coefficient γ_1^p in salt-free solutions (upper curve) with data (open circles) from Ref. 27, and of Eqs. (29) and (41) for the osmotic coefficient ϕ_p in salt-free solutions (lower curve) with data (filled circles) from Refs. 28 and 29.

exceptions, they may easily be summarized by stating that for values of b in the range 2.5–3.5 Å ($0.7 < \alpha < 1.0$ for vinylic polymers) values of γ_1^p fall between 0.20 and 0.35. According to Eq. (51b), the present theory predicts the value 0.21 when $b=2.5$ Å ($\xi=2.85$) and 0.30 when $b=3.5$ Å ($\xi=2.04$). In particular, Liquori *et al.*²⁵ found that γ_1^p was almost the same (0.21–0.25, insofar as the points may be read from their graphs) for fully neutralized NaPA, NaPES, and NaPP, all characterized by $b=2.5$ Å [theoretical value 0.21 from Eq. (51b)]. Usually, variation of γ_1^p with polyelectrolyte concentration n_e is reported to be small, although a tendency to decrease with decreasing n_e is frequently observed.^{17,23,24} In Fig. 5, the upper curve is computed from Eqs. (51a) and (51b). The data (open circles) are from Costantino *et al.*²⁷ The poor agreement for low values of ξ is probably due to the breakdown in the validity of the assumption of local rodlike structure.²⁷ The agreement for $\xi > 1$ is excellent.

As examples of the osmotic coefficient in salt-free solutions ϕ_p , one may compare the value 0.13 ($n_e=0.02N$) found by Alexandrowicz and Katchalsky¹⁶ for LiPP and NaPP ($\xi=2.85$) to the value 0.18 from Eq. (41). Data for NaPA and NaPMA are summarized by

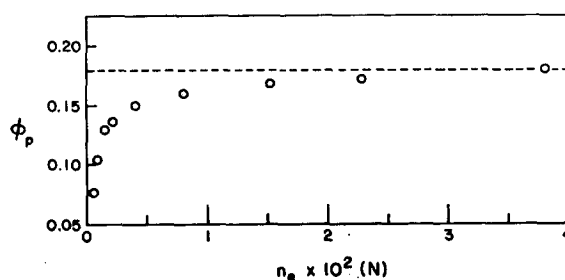


FIG. 6. Data for ϕ_p at low concentrations n_e compared to the value given by Eq. (41) (dashed line).

the filled circles^{28,29} in Fig. 5; the lower curve is drawn according to Eqs. (29) and (41). As for γ_1^p , the agreement is better for high charge densities than for low, probably because the cylindrically symmetric model is a poor description of the actual polymer configuration for small ξ .

Some recent measurements of ϕ_p by Takahashi, Kato, and Nagasawa³⁰ for the system NaPPS ($\xi=2.85$) are of considerable interest. In Fig. 6, these data are compared with the theoretical value $\phi_p=0.18$ (dashed line). For solutions more dilute than 0.005*N*, ϕ_p is observed to decrease sharply with further dilution. Above this concentration, the theoretical value is in excellent agreement with those observed.

The data of Takahashi *et al.* should be considered as a complement to those of Chu and Marinsky,³¹ who measured ϕ_p in salt-free PSS ($\alpha=0.92$) solutions for no less than nine counterions: H⁺, Li⁺, Na⁺, K⁺, Cs⁺, NH₄⁺ and the first three members of the tetraalkylammonium series—TMA⁺, TEA⁺ and TBA⁺. The lowest concentration used was $n_e=0.05N$; thus, Chu and Marinsky started where Takahashi *et al.* left off. In Figs. 1 and 2 of their paper, Chu and Marinsky plot ϕ_p as a function of n_e for each of the nine counterions and find that a linear extrapolation to $n_e=0$ is easily accomplished. In each case, the extrapolated value lies in the range 0.20–0.23. The theoretical value ($\xi=2.62$) from Eq. (41) is 0.19.

A unified interpretation of the measurements of Takahashi, Kato, and Nagasawa and of Chu and Marinsky based on the "limiting-law" concept is given in the next section.

VII. CONCLUDING REMARKS

On the basis of certain assumptions stated in Sec. II, formulas have been derived for colligative properties of polyelectrolyte solutions and shown to be frequently in quantitative agreement with experimental measurements (without the help of adjustable parameters). The formulas are thought to be "limiting laws" but in a restricted sense, a point which I wish to pursue further here with special reference to Fig. 6.

For an imaginary system of polyions which really are

infinitely long cylinders, the formulas give the limiting values (not the slopes) as the total mobile-ion concentration tends to zero. [For a solution which contains added simple salt, the ratio (n_e/n_s) must be fixed when the limit is taken.] For a real polyelectrolyte, these "limiting values" can still be observed, but only if the lowest mobile-ion concentration used is still sufficiently large for κ^{-1} to be less than l_0 , the average length of a local rodlike segment of the polyion chain. (Strictly speaking, κ should be calculated in this context from the concentration of uncondensed mobile ions, but such a distinction is not important for the order-of-magnitude arguments being presented.) Consider, for example, two charged groups separated by $(m-1)$ other charged groups along the chain. According to the model of an infinitely long cylinder (fully stretched chain) the distance between these groups is mb . Now if mb is sufficiently large to be comparable with l_0 , the actual average distance will be somewhat less than mb because of the globally flexible structure of the chain. This observation will be of no consequence as long as κ^{-1} is less than l_0 , for then the groups will be effectively screened; and I suggest that that is why the data in Fig. 6 for values of n_e larger than $5 \times 10^{-3}N$ reflect the predicted limiting value for an infinitely long, fully stretched chain, and also why the values of ϕ_p extrapolated from the high concentration range by Chu and Marinsky agree with the theoretical value. But as κ decreases and κ^{-1} becomes comparable to l_0 , interactions between these distant groups become important and are underestimated by the infinite cylinder model. Although the error is due to the deviation from cylindrical symmetry, these "end effects" may be formally treated by retaining the cylindrical symmetry and allowing b to become a function of κ which decreases with its argument. In Fig. 6, a value of b equal to about half that for a fully stretched chain [Eq. (3)] would give agreement with the measured value of ϕ_p when $n_e \approx 8 \times 10^{-4}N$. The deviation of this "adjusted" parameter b from the fixed value determined from Eq. (3) is a measure of how far the system deviates from the model of Sec. II.

ACKNOWLEDGMENTS

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²⁸ W. Kern, Z. Physik. Chem. **A184**, 197 (1939); also see Table I in Ref. 10.

²⁹ Z. Alexandrowicz, J. Polymer Sci. **40**, 91 (1959).

³⁰ A. Takahashi, N. Kato, and M. Nagasawa (private communication).

³¹ P. Chu and J. A. Marinsky, J. Phys. Chem. **71**, 4352 (1967).