

Limiting Laws and Counterion Condensation in Polyelectrolyte Solutions. 7. Electrophoretic Mobility and Conductance¹

Gerald S. Manning

Department of Chemistry, Rutgers University, New Brunswick, New Jersey 08903 (Received: November 11, 1980)

The theory of the electrophoretic mobility of a linear polyelectrolyte is developed in the context of the current model for counterion condensation theory. As in the classical theory of transport of charged objects in an applied electric field, two "effects" are crucial. Counterelectrophoresis of the solvent, designated here as the "charged-solvent" effect, is shown to be equivalent to screening of hydrodynamic interactions among chain segments. An "asymmetry field", traditionally called the relaxation field, arises from distortion of the Debye-Hückel ion atmosphere by the external field. Reasons are given for the break with traditional nomenclature. As an aid in forging continuity between the theory of the mobility and theories (not discussed here) for other transport modes, results are presented in terms of both the "electrophoretic friction coefficient" and the electrophoretic mobility. An additional, closely related result gives the electrical conductance of a polyelectrolyte solution. All expressions are restricted to the case of an ionic solution containing a single small electrolyte of general valence type with given ionic strength and infinitely dilute in polyelectrolyte component. The theory contains no adjustable parameters and therefore allows an extensive comparison of a priori prediction with measurement.

Introduction

A theoretical formula for the electrophoretic mobility of a linear polyelectrolyte molecule has been displayed and compared with some data.² The primary intent here is to derive that result, to improve it with a more complete description of the influence of the ion atmosphere, and then to provide a fairly extensive inspection of the relation of the improved formula to published measurements. A secondary purpose is to place the theory of the electrophoretic mobility more in the context of general transport theory by stressing the friction coefficient for translation of the center of mass. The two quantities are inversely related, and, because of coupling to the motion of the ion atmosphere, the various translational transport modes (unbiased thermal motion, diffusion along a concentration gradient, sedimentation, migration in an externally applied electric field) may not be uniquely characterized by a single friction coefficient.

In this paper only transport in an external electric field, or electrophoresis, is considered. For the relevant friction coefficient we propose the nomenclature *electrophoretic friction coefficient*. The electrophoretic friction coefficient is determined by two factors, interaction of the polyion with the solvent and interaction of the polyion with small ions. The former is in turn governed by two factors, friction intrinsic to the interaction of each structural unit of the polyion with the solvent and hydrodynamic interactions between pairs of units. Interaction with small ions may also be analyzed as the resultant of two effects, those of the locally charged solvent and the asymmetric ion atmosphere.³

At equilibrium the polyion is embedded in a time-averaged symmetric distribution of small ions, called its "atmosphere". In response to the charge on the central polyion, the atmosphere contains a higher density of counterions than of co-ions. The liquid in the atmospheric region is therefore charged oppositely to the charge residing on the polyion (more precisely, any force acting directly

on the small ions is transmitted to the solvent, so that the atmospheric volume as a whole behaves as though it were charged). In the presence of an externally applied electric field, the charged liquid is subjected to a volume force in a direction opposite to the migration, or drift, velocity of the polyion itself. The latter consequently moves against a local hydrodynamic flow and, accordingly, is slowed relative to its hypothetical drift in the absence of small ions. To first order this effect is independent of the field-induced asymmetry of the atmosphere.³ We propose the mnemonic nomenclature *charged-solvent effect* for what has been recognized from its standard description as the "electrophoretic effect". We advise against retention of the traditional phrase, which refers to the local electrophoresis of the *solvent*, in an area of research where emphasis is placed on the electrophoresis of the *polyion*.

When the electric field is applied, the oppositely charged and initially symmetric atmosphere is distorted in such a way that its charge density increases behind the polymer (i.e., on that side of the polymer opposite to where its drift velocity vector points) and decreases ahead of the polymer. The polymer is therefore subject to an internally created electric field directed oppositely to the external field; again, the polymer is slowed down. This field we propose to call the *asymmetry field*, since the traditional "relaxation field" not only is opaque but is a distinct misnomer as well. Here, a historical note may be of interest.

It is generally known that Debye and Hückel worked out a "limiting law", which turned out to be rigorously exact, for the free energy of a small-electrolyte solution.⁴ Only dimly recalled, however, is their companion paper,⁵ in which they presented a detailed calculation of the effects of charge on ionic migration velocities. Indeed, these authors correctly calculated the charged-solvent effect (although they did not fully appreciate its significance as a limiting law) and captured the essential features of the asymmetry effect. Their limiting law for ionic mobilities is inexact only because, for the latter, the standard mathematical apparatus used did not allow a self-consistent analysis of the Brownian motion of ions engaged in mutual interaction. By assuming a steady, nonfluctu-

(1) Work supported by the National Science Foundation, Grant No. DMR-7819289.

(2) G. S. Manning, *Q. Rev. Biophys.*, **11**, 179 (1978).

(3) R. M. Fuoss and F. Accascina, "Electrolytic Conductance", Interscience, New York, 1959.

(4) P. Debye and E. Hückel, *Phys. Z.*, **24**, 185 (1923).

(5) P. Debye and E. Hückel, *Phys. Z.*, **24**, 305 (1923).

ating velocity for the central ion directed along the external field and including Brownian motion only for the atmospheric ions, Debye and Hückel missed the reality that *both* the central ion and the atmospheric ions are subject to random thermal motion as well as to field-biased motion.

Onsager's great achievement⁶ was to improve the analysis of the asymmetry field with an extension of the mathematical tools of the day. With the introduction of binary distribution functions into a nonequilibrium context, he was able to solve exactly a difficult problem in Brownian motion theory and thereby to derive the rigorous limiting law which deservedly bears his name. Onsager's exact expression for the asymmetry field differs from Debye and Hückel's approximation in a proportionality factor involving the friction coefficients of the ions, which is generally too high in the approximate expression. By way of example, the Debye-Hückel result is too high by the numerical factor $2 - \sqrt{2}$ for a binary electrolyte solution with equal absolute values of the ionic valences and equal ionic friction coefficients. Additionally, Onsager greatly simplified the derivation of Debye and Hückel's correct result for the effect of the locally charged solvent and thus clarified its "limiting" nature as exact for vanishingly small ionic strengths.⁷

To return to the subject of nomenclature, it was on page 206 of their *equilibrium* paper⁴ that Debye and Hückel presented a qualitative description of the two classical velocity-diminishing ionic mechanisms. Their account of the electrophoretic, or charged-solvent, effect is correct, and we have essentially reproduced it above. But their description of the origins of the retarding internal field is misleading. They stated explicitly that this effect depends on the existence of a finite relaxation time for the construction of an ion atmosphere about a central ion suddenly immersed in the solution. Subsequent usage by others of "relaxation effect" thus became almost automatic. In fact, if one emphasizes the random thermal motion of the ions, that is, the mechanism of continuous destruction of the atmosphere as the central ion is continuously displaced by the field and continuously surrounds itself with a new atmosphere, it might indeed appear that if this continuous destruction and recreation of the atmosphere were instantaneous—if the relaxation time for the system were zero—then a steady-state atmospheric asymmetry could not be established, and the internal retarding field would be zero. If this argument were correct, the extent of asymmetry would be directly correlated with a time lag, and "relaxation field" would not be an inappropriate terminology.

That the argument is fallacious, however, may be seen from inspection of the actual mathematical expression for the retarding field, in either its earliest approximate form⁵ or its exact representation.^{3,6} The retarding field is a homogeneous function of order zero in the ionic friction coefficients. It does not vanish even if all of the friction coefficients are zero (zero relaxation time). The more rapid the relaxation of the atmosphere, the faster the central ion "outruns" it, thereby maintaining asymmetry. Or, again, if all of the ionic friction coefficients are set proportional to a single friction coefficient ζ , then ζ cancels from the expression for the retarding field, which therefore becomes independent of ζ regardless of how large or small it is (of how slow or fast is the relaxation). The establishment of a steady-state asymmetric distribution of countercharge about a central ion is not directly correlated with the relaxation time for formation of the equilibrium atmosphere.

The essential reason for the establishment of asymmetry is simply the tendency of the external field to separate the central ion from its oppositely charged atmosphere. It is this statement of the origin of the asymmetry field which describes the qualitative essence of either the approximate mathematical analysis of Debye and Hückel or the exact mathematical analysis of Onsager, even though the inclusion of Brownian motion in the mathematical description is requisite to its validity.

Theory

In the Introduction we noted four determinants of the electrophoretic friction coefficient f_E : the intrinsic hydrodynamic friction between a structural unit and the pure solvent, hydrodynamic interactions between units on the same polymer, the charged-solvent effect, and the asymmetry field. We consider these features in turn.

Intrinsic Friction. Let ζ denote the friction coefficient for a structural unit in pure solvent (no small ions). Let N be the number of units in each polymer chain. Then, in the absence of hydrodynamic interactions between units (complete free draining)

$$f_E = N\zeta \quad (1)$$

Moreover, in this approximation, the electrophoretic friction coefficient is not unique; the same coefficient describes translational friction for any center-of-mass transport.

Let Q be the absolute value of the total charge on the polyion. Then the electrophoretic mobility U , defined generally by

$$300U = Q/f_E \quad (2)$$

would obey the relation

$$300U = Q/(N\zeta) \quad (3)$$

In eq 2 the right-hand side is understood to be expressed in the cgs system of units, while U is expressed in the conventional mixed units $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, thus accounting for the unit conversion factor on the left-hand side. Since Q is proportional to N , eq 3 implies an electrophoretic mobility which is independent of molecular weight.

Hydrodynamic Interaction. Hydrodynamic interactions are included in a reasonably general expression given by Kirkwood⁸

$$f_E = N\zeta / \{1 + [\zeta / (6\pi\eta N)] \sum_{i=1}^N \sum_{\substack{j=1 \\ i \neq j}}^N \langle r_{ij}^{-1} \rangle\} \quad (4)$$

where r_{ij} is the distance between units i and j of the chain (regarded as point sources of friction), the average is over the internal chain coordinates, and η is the viscosity of pure solvent. This expression has been extensively studied.⁹ Again, it does not provide a friction coefficient unique to electrophoresis. The second term in the denominator accounts for hydrodynamic interactions between units; in its absence, eq 4 reduces to eq 1. If the electrophoretic mobility is formed in accordance with eq 2, the factor N in the numerator of f_E cancels the same factor implicit in Q , but the hydrodynamic interaction term in f_E provides a net molecular-weight dependence for U .

Charged-Solvent Effect. The charged-solvent effect acts on the hydrodynamic interaction term of eq 4. To see why, we review briefly the origin of this term in the context of the Oseen tensor formulation of hydrodynamics.⁹ Consider a force F acting at the center of a spherical volume element

(6) L. Onsager, *Phys. Z.*, **28**, 277 (1927).

(7) L. Onsager, *Phys. Z.*, **27**, 388 (1926).

(8) J. G. Kirkwood, *J. Polym. Sci.*, **12**, 1 (1954).

(9) V. A. Bloomfield, D. M. Crothers, and I. Tinoco, Jr., "Physical Chemistry of Nucleic Acids", Harper and Row, New York, 1974.

of liquid of radius r . The Stokes friction coefficient ζ , for this element is $6\pi\eta r$, so points on the boundary will have an average velocity $v_r = F/(6\pi\eta r)$. The situation is the same if the force acts directly on a structural unit of a polymer at the center of the volume element; v_r is now the velocity imparted to another structural unit situated on the boundary surface (i.e., to any unit at distance r from the unit at the center). Now any given unit i is on a set $\{j\}$ of such boundary surfaces, an element j of the set being the surface of the spherical volume of radius r_{ij} containing polymeric unit j at its center. The velocity imparted to the given unit i due to forces F acting on the other $N-1$ units is therefore equal to $F \sum_{j=1}^N (6\pi\eta r_{ij})^{-1}$, with the term $j=i$ deleted. The sum acts as the reciprocal of a composite effective friction coefficient.

Such considerations provide the physical basis for eq 4, which may be schematically written as

$$f_E/N = \zeta/[1 + (\zeta/\zeta_{\text{eff}})] \quad (5)$$

where an effective value

$$\zeta_{\text{eff}} = 1/[N^{-1} \sum_{i=1}^N \sum_{j=1, j \neq i}^N \langle (6\pi\eta r_{ij})^{-1} \rangle] \quad (6)$$

characterizes the hydrodynamic influence of *other* units on a given unit, which, when isolated, has friction coefficient ζ . If the influence is small (small N , large average r_{ij}), then $\zeta_{\text{eff}} \gg \zeta$ and $f_E/N = \zeta$; if hydrodynamic interactions dominate, $\zeta_{\text{eff}} \ll \zeta$, so $f_E/N = \zeta_{\text{eff}}$. In the latter case the friction coefficient ζ intrinsic to an isolated unit is a negligible factor.

Now consider the case for which each unit is a point bearing a charge of absolute value Q_1 , each of the same sign, so that the total polymeric charge is

$$Q = NQ_1 \quad (7)$$

In a first attempt to lay bare the physical essentials, each unit may be portrayed as at the center of a thin spherical shell containing the charge $-Q_1$ uniformly distributed. The radius of the shell is the Debye screening length κ^{-1} , defined by eq 8, where q is the protonic charge, ϵ the bulk dielectric

$$\kappa^2 = [4\pi q^2/(\epsilon k_B T)] \sum_k (10^{-3} L_{Av} c_k) z_k^2 \quad (8)$$

constant of the solvent, k_B Boltzmann's constant, T the Kelvin temperature, L_{Av} Avogadro's number, c_k the molarity of (uncondensed) small ions of species k , and z_k their valence. The collection of shells is a primitive representation of the ion atmosphere enveloping the polyion. The concentrations c_k in eq 8 are assumed to satisfy electroneutrality among themselves, so the system being investigated is a small-electrolyte solution to which an isolated polyion is added (excess-salt condition).

Consider first a single unit (point charge Q_1) in isolation from all others. In an external electric field E it would migrate with velocity $v = \zeta_0^{-1} Q_1 E$ were it not for the effect of its atmosphere, which migrates in the opposite direction, together with the solvent in its interior, with velocity $v' = (6\pi\eta\kappa^{-1})^{-1} Q_1 E$. The net velocity of the polymeric unit at its center, therefore, is $v - v' = [1 - \zeta_0\kappa/(6\pi\eta)] \zeta_0^{-1} Q_1 E$. Curiously, in view of the primitive picture of the atmosphere, this result is exact for the limiting form of the charged-solvent (electrophoretic) effect on the mobility of a small ion in a dilute small-ion electrolyte solution.³ We take, then, for the friction coefficient ζ of our polyionic unit

$$\zeta = \zeta_0[1 + \zeta_0\kappa/(6\pi\eta)] \quad (9)$$

Next we inquire about the hydrodynamic influence of unit j on unit i . Suppose i is located within the atmos-

pheric shell of j , that is, the distance between i and j is less than κ^{-1} . Then the presence of the atmosphere does not affect the hydrodynamic influence of the velocity of j on the velocity of i . But suppose the distance of j from i is greater than κ^{-1} , so that i lies outside the atmosphere of j . Recall that the average velocity at the position of i induced by a force F on the spherical volume of radius r_{ij} with j at its center is $F/(6\pi\eta r_{ij})$. But this force is zero, since it equals charge \times field, and the charge inside the volume is zero (or at least that part of the charge associated with j and its atmosphere, the possible portion belonging to the atmosphere of i having already been considered). Thus, in an expression such as eq 6, r_{ij}^{-1} would have to be weighted with the factor zero in taking the average for values of r_{ij} greater than κ^{-1} .

It is a routine exercise in the exact Debye-Hückel equilibrium limiting theory to show that the amount of charge in a spherical volume element of radius r centered on the position of an ion of valence z is $zqe^{-\kappa r}(1 + \kappa r)$ or, in the dilute limit, $zqe^{-\kappa r}$. For large r ($\kappa r \gg 1$) the continuous charge density of the atmosphere completely neutralizes the charge on the central ion, but for small r ($\kappa r \ll 1$) the volume element contains negligibly less than the charge on the central ion. To handle the real atmosphere, therefore, as opposed to its primitive idealization, we must weight r_{ij}^{-1} with the factor $e^{-\kappa r_{ij}}$:

$$\zeta_{\text{eff}} = 6\pi\eta/[N^{-1} \sum_{i=1}^N \sum_{j=1, j \neq i}^N \langle r_{ij}^{-1} e^{-\kappa r_{ij}} \rangle] \quad (10)$$

Because long-range hydrodynamic interactions are now "screened" with characteristic length κ^{-1} , we may neglect interactions between polymeric charges located far apart along the flexible chain, since they will only rarely approach within the distance κ^{-1} . Further, we may assume that stretches of the chain of length comparable to κ^{-1} are almost fully extended because of the nearly unscreened electrostatic repulsions among polymeric charges within this length. Therefore, in eq 10 we may take r_{ij} equal to the constant value $|i - j|b$, where b is the polymeric charge spacing along the contour length, and dispense with averages. The resulting double sum is closely related to what has appeared in another context in polyelectrolyte theory,^{2,10} in the limit

$$\kappa b \ll 1 \quad (11)$$

the result for f_E , given by eq 5 and 10, is

$$f_E = N\zeta/[1 + [\zeta/(3\pi\eta b)]|\ln(\kappa b)|] \quad (12)$$

where ζ is given by eq 9. To avoid confusion,⁹ we stress again that b here is the polyion charge spacing and not the diameter of a spherical bead taken as a frictional unit; thus the expression $3\pi\eta b$ is *not* a Stokes representation for ζ , the frictional unit here having been modeled by a point charge.

Equation 12 must be further reduced in accordance with the restriction expressed by inequality 11. Although ζ is not equal to $3\pi\eta b$, these two quantities must be of the same order in any reasonable representation. Hence

$$f_E = 3\pi\eta Nb|\ln(\kappa b)|^{-1} \quad (13)$$

The quantity Nb is precisely the contour length of the polymer, so the friction coefficient, proportional to the molecular weight, is "free-draining". Yet the friction coefficient ζ of a structural unit has cancelled, $\zeta_{\text{eff}} \ll \zeta$ (see eq 5), which indicates the dominance of hydrodynamic

interactions. The resolution of this puzzle is that hydrodynamic interactions between segments of the chain distant along the contour are absent, but they do dominate the friction within each locally rodlike segment.

To pass from f_E to the electrophoretic mobility requires a value for the polymeric charge Q consistent with use of the Debye-Hückel equilibrium theory, which in this case involves superposition of Debye-Hückel interactions (i.e., superposition of spherically symmetric Debye-Hückel atmospheres) along the chain of closely spaced charges. It has been shown^{2,11} that such superposition is consistent with a unique unit charge

$$Q_1 = |z_1|^{-1} \xi^{-1} q \quad (14)$$

if, as is usually the case, $\xi \geq |z_1|^{-1}$, and if the structural charge on each unit is monovalent, i.e., $\pm q$. In writing eq 14 we assume as well that only one species of counterion is present, species 1, with valence z_1 . The familiar linear charge density parameter is defined to lack dimensions

$$\xi = q^2 / (\epsilon k T b) \quad (15)$$

The point is that stability within Debye-Hückel superposition is achieved only if sufficiently many counterions condense on the polymer to lower each structural charge q to the value of eq 14. Then, from eq 7

$$Q = N |z_1|^{-1} \xi^{-1} q \quad (16)$$

Equations 2, 13, and 16 combine to give the result stated previously² (with a different notation for counterion valence)

$$300U = |z_1|^{-1} [\epsilon k T / (3\pi\eta q)] |\ln(\kappa b)| \quad (17)$$

where eq 15 has also been used.

Asymmetry Field. In a previous publication¹² false reasoning, for which I was responsible, led to the incorrect conclusion that the asymmetry effect is negligible if the equivalent concentration of electroneutral polyelectrolyte component is small relative to that of the small-electrolyte component (excess added salt). Regardless of relative or absolute concentrations, a polyion in solution is surrounded by an oppositely charged atmosphere with spatial disposition perturbed from the symmetrical by an external electric field. In the absence of added salt, however, we were able to calculate an asymmetry field by noting the equality dictated by Newton's third law between the internal electric fields acting on the counterions and on the polyion.¹³ This procedure has been validated by the irreversible thermodynamic treatment of Schmitt et al.¹⁴ If a small-electrolyte salt is added, the force balance involves co-ions as well as counterions. Fortunately, Schmitt et al. worked out the general case,¹⁵ and we are now able to calculate the required self-consistent field in the excess-salt limit usually sought in experiments.

We begin again with an isolated polymeric unit, the point of charge with absolute value Q_1 . Instead of eq 9, ζ must satisfy a formula accounting for the asymmetry, as well as the charged-solvent effect. For this purpose we take the Onsager limiting law, but, since ζ cancels from our final result anyway, we write it simply in the form

$$\zeta = \zeta_0(1 + a\kappa) \quad (18)$$

where a is independent of ionic strength.

The analysis of the asymmetry effect on the entire polymer rests heavily on the following expressions for the small-ion fluxes J_i (mol cm⁻² s⁻¹):¹⁶

$$J_i / (10^{-3} c_i E) = (D_i / D_i^s) (|z_i| q / \zeta_i^s) = (Q / f_E) [1 - (D_i / D_i^s)] \quad (19)$$

We have specialized to the case of a single added salt, with species 1 the same as the polyelectrolyte counterion and species 2 the co-ion. Equation 19 is written for $i = 1, 2$; the upper sign applies to $i = 1$, the lower to $i = 2$. The quantity D_i is the self-diffusion coefficient of (uncondensed) ions of species i in the polyelectrolyte solution; D_i^s is its value in the absence of polyelectrolyte component but in solution of the same small-electrolyte concentration. Similarly, ζ_i^s is the friction coefficient (electrophoretic) in the polyelectrolyte-free, small-salt solution. In previous publications we were careful to derive such relations in the limit of very low small-electrolyte concentrations, where use of the limiting values D_i^0 and ζ_i^0 is rigorous. Dispensing with the niceties of a minor point, we justify the presence of D_i^s and ζ_i^s in eq 19 with the observation that the correct polyelectrolyte-free result is obtained on setting $D_i = D_i^s$.

The expression $|z_i| q / \zeta_i^s$ is the electrophoretic mobility u_i^s of small ion i in cgs units. We factor it, obtaining eq 20. If there is no polyelectrolyte, the left-hand side equals

$$J_i / (10^{-3} c_i u_i^s E) = 1 - [1 - (D_i / D_i^s)] [1 \pm Q / (f_E u_i^s)] \quad (20)$$

unity. Moreover, the derivation of eq 19 makes it clear that the effect of the polyion evident in eq 20 is in fact an asymmetry effect.¹⁶ Designating by ΔE_{ip} the internal field generated by Coulomb interactions between polyion and asymmetric atmosphere and acting upon small ions i , we have

$$\Delta E_{ip} / E = [1 - (D_i / D_i^s)] [1 \pm Q / (f_E u_i^s)] \quad (21)$$

Parenthetically, we note that the charged-solvent effect, ignored in the development of eq 19, is expected to be small (as manifested in small-ion fluxes), since the net charge in the volume outside any small ion is equal in magnitude merely to that on the small ion. By contrast, the asymmetry effect on J_i can be large because it involves the effect of the large polyionic field on the Brownian motion of a small ion. This consideration appears to be supported by the irreversible thermodynamic analysis of Schmitt et al. (see their eq 25 and related discussion).¹⁴

We introduce the quantity X (eq 22), used here as a

$$X = N c_p / c_s \quad (22)$$

small expansion parameter. The concentration c_p is of polyion molecules, so that the numerator is the equivalent concentration of electroneutral polyelectrolyte component, while c_s is the concentration of small electrolyte component. Generalizing a previous result¹⁶ to arbitrary values of z_1 and z_2 , we get to first order in X

$$1 - (D_i / D_i^s) = \frac{1}{3} z_i^2 (\nu_1 + \nu_2)^{-1} |z_1 z_2|^{-1} \xi X \quad (23)$$

where ν_i is the number of ions of species i in the formula for the small electrolyte (e.g., $\nu_1 = 1$, $\nu_2 = 2$ for MgCl₂ and a polyanion). This formula is valid for ξ less than or equal to the critical value for counterion condensation, or $|z_1|^{-1}$. For the case of primary interest, however, $\xi > |z_1|^{-1}$, so that the net value of ξ , account taken of condensed counterions, is $|z_1|^{-1}$. But it is precisely this net value which should be

(11) G. S. Manning, *Acc. Chem. Res.*, **12**, 443 (1979).

(12) P. D. Ross, R. L. Scruggs, and G. S. Manning, *Biopolymers*, **14**, 1991 (1975).

(13) G. S. Manning, *J. Phys. Chem.*, **79**, 262 (1975).

(14) A. Schmitt, J. P. Meullenet, and R. Varoqui, *Biopolymers*, **17**, 413 (1978).

(15) A. Schmitt, J. P. Meullenet, and R. Varoqui, *Biopolymers*, **17**, 1249 (1978).

(16) D. I. Devore and G. S. Manning, *J. Phys. Chem.*, **78**, 1242 (1974).

(17) G. S. Manning, *J. Chem. Phys.*, **51**, 934 (1969).

used in eq 23, since only the effect of the polyion on the atmospheric ions is desired. With ξ replaced by $|z_1|^{-1}$, eq 23 becomes

$$1 - (D_i/D_i^s) = \frac{1}{3}(z_i/z_1)^2|z_2|^{-1}(\nu_1 + \nu_2)^{-1}X \quad (24)$$

Hence, to first order in X

$$\Delta E_{ip}/E = \frac{1}{3}(z_i/z_1)^2|z_2|^{-1}(\nu_1 + \nu_2)^{-1}[1 \pm Q/(f_E u_i^s)]X \quad (25)$$

Formulas given by Schmitt et al.¹⁵ relate $-\Delta E_{ip}$, the internal polyion field acting on ions i , to $-\Delta E_{pi}$, the contribution of ions i to the internal field acting on the polymer. To first order in X , these authors show that a consistent force balance requires

$$\Delta E_{ip} = \pm(\nu_1|z_1|)^{-1}X\Delta E_{pi} \quad (26)$$

where, again, the upper sign pertains to $i = 1$ and the lower to $i = 2$. With eq 25 for the left-hand side of eq 26

$$\Delta E_{pi}/E = \pm \frac{1}{3}z_i^2|z_1z_2|^{-1}\nu_1(\nu_1 + \nu_2)^{-1}[1 \pm Q/(f_E u_i^s)] \quad (27)$$

The total asymmetry field acting on the polyion is the negative of ΔE_p

$$\Delta E_p = \Delta E_{p1} + \Delta E_{p2} \quad (28)$$

or

$$\Delta E_p/E = \frac{1}{3}\nu_1(\nu_1 + \nu_2)^{-1}|z_1z_2|^{-1}[(z_1^2 - z_2^2) + (Q/f_E) \times (z_1^2/u_1^s + z_2^2/u_2^s)] \quad (29)$$

By definition of f_E the migration velocity v of the polyion satisfies the relation

$$v = (Q/f_E)E \quad (30)$$

Define E^* as the actual field operating on the polyion

$$E^* = E - \Delta E_p \quad (31)$$

and f_E^* as the electrophoretic friction coefficient in the absence of the asymmetry field. Then the same velocity v may be written as

$$v = (Q/f_E^*)E^* \quad (32)$$

so

$$f_E = f_E^*/[1 - (\Delta E_p/E)] \quad (33)$$

In this formula we use eq 29 for $\Delta E_p/E$ and the right-hand side of eq 13, which gives precisely the electrophoretic friction coefficient influenced by the locally charged solvent but not by asymmetry, for f_E^* . The result is eq 34.

$$f_E = (Nb)[3\pi\eta][\ln(\kappa b)]^{-1} + \frac{1}{3}\nu_1(\nu_1 + \nu_2)^{-1}z_1^{-2}|z_2|^{-1}(\epsilon kT/q)(z_1^2/u_1^s + z_2^2/u_2^s)/[1 - \frac{1}{3}\nu_1(\nu_1 + \nu_2)^{-1}|z_1z_2|^{-1}(z_1^2 - z_2^2)] \quad (34)$$

Equations 15 and 16 have been used for ξ and Q in writing this formula for f_E , in which the first term in the numerator may be recognized as incorporating the charged-solvent effect while the other terms represent the asymmetry field. The prefactor is the contour length of the polymer, to which the electrophoretic friction coefficient is proportional.

The electrophoretic mobility is obtained from eq 2, 16, and 34 in an unwieldy form best written as

$$300U = (300U^*)(\alpha/\beta) \quad (35)$$

where $300U^*$ contains only the charged-solvent effect and is given by the right-hand side of eq 17.

$$300U^* = |z_1|^{-1}[\epsilon kT/(3\pi\eta q)][\ln(\kappa b)] \quad (36)$$

$$\alpha = 1 - \frac{1}{3}\nu_1(\nu_1 + \nu_2)^{-1}|z_1z_2|^{-1}(z_1^2 - z_2^2) \quad (37)$$

while

$$\beta = 1 + 108\nu_1(\nu_1 + \nu_2)^{-1}|z_1z_2|^{-1}(300U^*)(z_1^2/\lambda_1^s + z_2^2/\lambda_2^s) \quad (38)$$

The strange-looking numerical factor 108 in the formula for β originates in the conversion from the electrophoretic mobilities u_i^s of the small ions to ionic conductances λ_i^s ; it is a universal constant.¹⁸

As a final result in this section we record a formula for the specific conductance of a polyelectrolyte solution under excess-salt conditions. The usual symbol for specific conductance is κ , but, to avoid confusion with the Debye screening parameter, let K be the specific conductance of the polyelectrolyte solution and K_s that of the corresponding small-electrolyte solution, with $K \rightarrow K_s$ as the polyion concentration vanishes. Define

$$K_p = K - K_s \quad (39)$$

Then, if the small electrolyte is present in excess, so that K_p is linear in the polyelectrolyte concentration

$$K_p = 10^{-3}A_pC_p \quad (40)$$

where C_p is the stoichiometric molarity of monovalent groups on the polyion (i.e., $C_p = Nc_p$), and

$$A_p = |z_1|^{-1}\xi^{-1}[(Bt_1^s + B)\lambda_s + B\lambda_p] \quad (41)$$

where t_1^s is the transference number of the counterion in the small-electrolyte solution, λ_s is the equivalent conductance of the small-electrolyte solution, and λ_p is the equivalent ionic conductance of the polyion. The two constants are given by

$$B = 1 - \frac{1}{3}\nu_2(\nu_1 + \nu_2)^{-1}(z_1^2 - z_2^2)z_1^{-2} \quad (42)$$

$$B' = -\frac{1}{3}\nu_2(\nu_1 + \nu_2)^{-1}(z_2/z_1)^2 \quad (43)$$

The quantities t_1^s and λ_s are to be obtained from standard compilations, while

$$\lambda_p = FU \quad (44)$$

where F is the Faraday constant (9.65×10^4 C/equiv) and U is the electrophoretic mobility of eq 35. This result is restricted to $\xi > |z_1|^{-1}$ and generalizes a previous result¹² to arbitrary values for the small-ion valences. Additionally, eq 41 incorporates the improved result obtained here for U into the formula for λ_p .

Comparison with Experiment

Our formula for the electrophoretic mobility, eq 35–38, is an interesting one, inasmuch as there is a predicted dependence on a variety of parameters (none of them adjustable). U depends on solvent dielectric constant, solvent viscosity, ionic strength (κ), polymer charge spacing (b), salt type (ν_i, z_i), and the transport characteristics of the salt (λ_i^s). There is a notable absence of dependence on molecular weight. We review some of the available data and compare them with theory.

*Data of Olivera, Baine, and Davidson.*¹⁹ The cited authors measured U for DNA as a function of molecular weight, ionic strength, pH titration charge, and conformation. All data were collected in aqueous buffered NaCl at 0 °C.

(18) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Butterworths, London, 1959.

(19) B. M. Olivera, P. Baine, and N. Davidson, *Biopolymers*, **2**, 245 (1964).

TABLE I: Correlation of Theory with Data from Olivera et al.¹⁹

c_{NaCl}, M	native DNA		denatured DNA	
	$10^4 \times U_{\text{obsd}}$	$10^4 \times U_{\text{theory}}$	$10^4 \times U_{\text{obsd}}$	$10^4 \times U_{\text{theory}}$
0.004	2.34	3.14	2.06	2.49
0.01	2.17	2.83	1.90	2.12
0.10	1.51	1.92	1.33	1.01

TABLE II: Correlation of Theory with Data from Olivera et al.¹⁹

DNA sample	pH	titration charge	mobility ratio	
			obsd	theory
calf thymus, native	4.10	-0.75	0.90	0.93
T-4, native	4.57	-0.89	0.94	0.97
T-4, native	4.10	-0.82	0.90	0.95
calf thymus, denat	4.10	-0.52	0.90	1.00

In 0.01 M NaCl measured mobilities were independent of molecular weight over the range investigated, from 1×10^6 to 130×10^6 , both for native and denatured DNA (authors' Table I). In 0.1 M NaCl independence of molecular weight was verified over a 10-fold range, although the data are much more sparse (authors' Table III). These observations agree with the prediction of our theory (and of other theories; see below). The monomer, however, was observed to have a substantially lower mobility than single-stranded DNA, in agreement with our result that the polyion mobility reflects *polyelectrolyte* behavior (principally the $\ln(\kappa b)$ dependence).

Table I compares predicted and observed values of the mobility as a function of ionic strength both for native and denatured DNA. For the ionic conductances λ_i^s in eq 38 we used the limiting values λ_i^0 in pure water instead of at the corresponding small-electrolyte concentration. Estimates suggest only a small difference in the result (in the second decimal place). Moreover, the approximations used in the theory do not justify retention of concentration effects in λ_i^s which would multiply the limiting form $\ln(\kappa b)$ in U^* . Unless stated otherwise, all subsequent calculations utilize λ_i^0 also. For native DNA, $b = 1.7 \text{ \AA}$; for denatured DNA (if single-stranded), $b = 4.3 \text{ \AA}$ at the pH of the measurements, 7.50.²⁰ Note from Table I that both theory and observation indicate the mobility as increasing with decreasing ionic strength for the two conformations. Moreover, both theory and measurement agree that denatured DNA has a lower mobility than native DNA at any given ionic strength.

Table II shows the dependence of mobility on pH. The point made by Olivera et al. was that the mobility decreases less than would be expected if it were simply proportional to the structural charge on the polymer (which becomes less negative as protons are bound at lower pH). This observation is supported by the theoretical formula for U , which is clearly not proportional to the structural charge. According to the theory, the quantity changed as protons are bound is b , the average charge spacing. For example, if the titration charge (third column of Table II) is -0.75 (per monomer nucleotide), then b is increased from 1.7 \AA (titration charge -1.00 at neutral pH) to $(1.7)(0.75)^{-1} = 2.3 \text{ \AA}$. Since larger values of b imply lower mobilities (according to the theory), the ratio of the mobility at low pH to that at neutral pH (last two columns of Table II) is less than unity, but by no means in proportion to the titration charge.

TABLE III: Correlation of Theory with Data from Ross and Scruggs²¹

c_{MCl}, M	$10^4 U_{\text{obsd}}/10^4 U_{\text{theory}}$		
	Li^+	Na^+	K^+
0.05	1.87/2.19	1.99/2.30	
0.10	1.63/1.91	1.85/2.00	
0.20	1.34/1.61	1.55/1.67	1.84/1.73
0.40	1.07/1.28	1.21/1.31	

TABLE IV: Correlation of Theory with Data from Hartford and Flygare²⁴

c_{NaCl}, M	$10^4 \times U_{\text{obsd}}$	$10^4 \times U_{\text{theory}}$	c_{NaCl}, M	$10^4 \times U_{\text{obsd}}$	$10^4 \times U_{\text{theory}}$
0.004	5.9	5.4	0.05	3.3	3.9
0.01	5.0	4.9	0.10	2.8	3.3
0.02	4.4	4.5			

The prediction for denatured calf thymus DNA (last row of Table II), which does not agree well with observation, is exceptional. It was calculated as follows. For denatured DNA at pH 4.10, b has been estimated at 2.2 \AA based on the phosphate spacing alone.²⁰ This value, much lower than that ($\sim 4 \text{ \AA}$) at neutral pH, possibly reflects folding of the single strand on itself induced by the low net structural charge at low pH. For the indicated titration charge of -0.52, the value of b required by the theory is $\text{ca. } (2.2 \text{ \AA})(0.52)^{-1} = 4.2 \text{ \AA}$, which is the same as at neutral pH—hence the calculated value of unity for the mobility ratio.

*Data of Ross and Scruggs.*²¹ These authors measured the electrophoretic mobility of DNA at 1.3°C as a function of ionic strength c_{MCl} in several metal chlorides. Since the binding of tetramethylammonium ion to DNA is atypical,^{22,23} we restrict attention to $\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+$. For each salt Table III confirms the ionic-strength dependence of the mobility; the polyion drifts more slowly in an electric field in more concentrated salt solutions. There is a dependence on cation species: $U(\text{Li}^+) < U(\text{Na}^+) < U(\text{K}^+)$. The conventional explanation has been that Li^+ neutralizes more phosphate charge by specific site binding than does Na^+ , and Na^+ more than K^+ . The theory, however, explicitly states that the same amount of phosphate charge is neutralized by all three (see eq 14). The sequence specificity predicted by the theory, which is the same as that observed, is due to the inequality of the λ_i^0 : $\lambda_{\text{Li}^+}^0 < \lambda_{\text{Na}^+}^0 < \lambda_{\text{K}^+}^0$. In other words the cation specificity in the theory is caused by the different transport characteristics of different small-electrolyte solutions; it has nothing to do with even the *presence* of polyelectrolyte, let alone a specific site interaction between polyion and cation. In a previous paper² I speculated on another possibility underlying cation specificity, but I am now inclined toward abandoning that discussion. It should, however, be noted that the quantitative extent of specificity predicted here is somewhat less than observed (except at the lowest ionic strength, where the theory is presumably most accurate, and where the quantitative extent of agreement is quite good).

*Data of Hartford and Flygare.*²⁴ Using the recently developed technique of electrophoretic light scattering, stated by the authors to be more accurate at low ionic strength than the conventional moving boundary, measurements of native DNA mobility in NaCl at 20°C were

(21) P. D. Ross and R. L. Scruggs, *Biopolymers*, **2**, 231 (1964).(22) G. de Murcia, B. Wilhelm, F. X. Wilhelm, and M. P. Daune, *Biophys. Chem.*, **8**, 377 (1978).(23) L. A. Marky, D. Patel, and K. J. Breslauer, *Biochemistry*, in press.(24) S. L. Hartford and W. H. Flygare, *Macromolecules*, **8**, 80 (1975).(20) M. T. Record, Jr., C. P. Woodbury, and T. M. Lohman, *Biopolymers*, **15**, 893 (1976).

TABLE V: Correlation of Theory with Data from Papon and Strauss^a

$c_{\text{MgCl}_2}, \text{M}$	$10^4 \times U_{\text{obsd}}$	$10^4 \times U_{\text{theory}}$	$c_{\text{MgCl}_2}, \text{M}$	$10^4 \times U_{\text{obsd}}$	$10^4 \times U_{\text{theory}}$
2.8×10^{-4}	1.6 ± 0.2	1.89	1.6×10^{-2}	0.76	1.07
5.0×10^{-4}	1.5 ± 0.2	1.78	3.1×10^{-2}	0.60	0.92
2.6×10^{-3}	1.00	1.46	9.5×10^{-2}	0.45	0.65
5.5×10^{-3}	0.86	1.30			

^a Unpublished.TABLE VI: Correlation of Theory with Data from Strauss et al.^{25,26}

M^+ ($c_{\text{MBr}} = 0.2 \text{ M}$)	$10^4 \times U_{\text{obsd}}$	$10^4 \times U_{\text{theory}}$	M^+ ($c_{\text{MBr}} = 0.2 \text{ M}$)	$10^4 \times U_{\text{obsd}}$	$10^4 \times U_{\text{theory}}$
Li^+	1.23	1.19	K^+	1.41	1.25
Na^+	1.14	1.22	$(\text{CH}_3)_4\text{N}^+$	2.07	1.21

performed (Table IV). The usual ionic-strength dependence is confirmed. In addition the authors recorded a data point for denatured DNA in 0.01 NaCl, pH 7.0, at 20 °C. Their result for $(10^4 U_{\text{native}}/10^4 U_{\text{denat}})$ is 5.0/4.2, while our prediction is 4.9/3.7; $b = 4.1 \text{ \AA}$ at pH 7.0 for the single strand.²⁰

Data of Papon and Strauss. I am grateful to U. P. Strauss for allowing me to use the unpublished data collected by Dr. Papon in his laboratory for the system (aqueous MgDNA–MgCl₂, 0 °C). In a previous article² we compared these data with a formula lacking the asymmetry effect, i.e., with U^* . The predictions were uniformly too high by a factor of ~ 2 . Table V indicates considerable improvement due to inclusion of the asymmetry effect. Comparison with Table I shows that both theory and measurement indicate mobilities in MgCl₂ substantially lower than in NaCl. The dominant reason according to theory is the greater extent of phosphate neutralization by the divalent cation (see eq 14).

Not discussed here is the interesting observation by Papon and Strauss of a charge reversal at higher concentration of MgCl₂ than that listed in Table V; under these conditions DNA migrates like a cation.

Data of Strauss et al.^{25,26} In a set of two papers Strauss and his colleagues studied the electrophoresis of polyphosphate at 0 °C. They observed no dependence on molecular weight. Table VI illustrates some results; all entries pertain to 0.2 M aqueous MBr, where M^+ is a univalent cation. For Li^+ and Na^+ the theory provides reasonable agreement with data.

Observed values are significantly higher than predicted in KBr and much higher in $[(\text{CH}_3)_4\text{N}]\text{Br}$. That this phenomenon may be related to the high salt concentration, 0.2 M, is indicated by results at 0.01 M, where measured values of $10^4 U$ for NaBr and $[(\text{CH}_3)_4\text{N}]\text{Br}$ are both 2.0, compared to the predicted values, 2.56 and 2.52, for these salts, respectively (λ_+^0 is almost the same for these two cations).

Comparison of Tables III and VI for DNA and polyphosphate, respectively, (λ_{Cl}^0 and λ_{Br}^0 are almost the same) shows that the mobility of the former is greater than that of the latter. For example, the observed ratio for 0.2 M Li^+ is 1.09, compared to the predicted value 1.35; for Na^+ , observed ratio/predicted ratio = 1.36/1.37; and for K^+ , 1.30/1.38. The theoretical explanation is the difference between the charge spacings; $b_{\text{DNA}} = 1.7 \text{ \AA}$, $b_{\text{PP}} = 2.5 \text{ \AA}$.

TABLE VII: Correlation of Theory with Data from Meullenet et al.²⁷

α	$10^4 \times U_{\text{obsd}}$	$10^4 \times U_{\text{theory}}$	α	$10^4 \times U_{\text{obsd}}$	$10^4 \times U_{\text{theory}}$
0.4	2.7	1.7	0.7	4.1	2.7
0.5	3.3	2.1	0.8	4.1	2.9
0.6	3.6	2.4	0.9	4.5	3.1

TABLE VIII: Correlation of Theory with Data from Meullenet et al.²⁷

$c_{\text{NaBr}}, \text{M}$	$10^4 \times U_{\text{obsd}}$	$10^4 \times U_{\text{theory}}$	$c_{\text{NaBr}}, \text{M}$	$10^4 \times U_{\text{obsd}}$	$10^4 \times U_{\text{theory}}$
0.01	5.0	3.7	0.05	3.1	2.4
0.02	4.5	3.2	0.10	2.3	1.8
0.03	3.9	2.9			

TABLE IX: Correlation of Theory with Conductance Data from Ross and Scruggs¹²

c_{MCl}, M	MCl	$A_p(\text{obsd})$	$A_p(\text{theory})$
0.01	LiCl	7.4	9.7
	NaCl	12.8	11.7
0.02	LiCl	8.5	9.1
	NaCl	9.2	11.0
	KCl	11.8	14.8
0.05	LiCl	3.6	8.2
	NaCl	9.4	10.1
	KCl	14.6	13.7

*Data of Meullenet, Schmitt, and Drifford.*²⁷ The authors measured the mobility of a synthetic alternating copolymer of maleic acid and ethyl vinyl ether in aqueous NaBr by electrophoretic light scattering at 20 °C. The distinguishing feature of this polymer is its weak-acid property; its charge spacing b may be easily varied over a wide range. Independence of mobility on molecular weight was confirmed. Table VII compares measured and predicted dependencies on b ; the quantity α is the degree of neutralization of the weak acid, $b = (2.5 \text{ \AA})\alpha^{-1}$. The NaBr concentration in this series is 0.05 M. Theoretical values are somewhat below those observed, but the differences are essentially constant, indicating close parallelism of the trends.

It is interesting that the authors expected to find no dependence of U on α in the range shown, which is characterized by values of ξ greater than the critical value of unity for univalent counterion condensation. The reasoning, with which I would have agreed at the time they wrote their paper, is that the total polymeric charge Q given by eq 16 is constant over the range (set $z_1 = 1$, $N = \alpha N_1$, $\xi = \alpha \xi_1$, where "subscript 1" refers to values at full acid neutralization $\alpha = 1$). The present theory is sufficiently complex, however, to provide for an electrophoretic mobility not proportional to Q .

Table VIII shows a typical dependence on NaBr concentration with α fixed at 0.6.

*Conductance Data of Ross and Scruggs.*¹² In Table IX are listed measured values of A_p obtained at 5 °C for DNA by substituting measured values of K (in the linear region) and K_s into eq 39 and 40. The listed theoretical values were obtained from eq 41–43. Limiting (zero concentration) values were used for t_1^s and λ_s , since, as with similar small-electrolyte quantities in the theory for U , higher-order concentration corrections are inconsistent with the order retained for λ_p . A spot check suggests that inclusion of such corrections produces theoretical values differing from those listed to within the experimental precision of the measured values. With the exception of the entry for

(25) U. P. Strauss, D. Woodside, and P. Wineman, *J. Phys. Chem.*, **61**, 1353 (1957).(26) U. P. Strauss and P. D. Ross, *J. Am. Chem. Soc.*, **81**, 5296 (1959).(27) J. P. Meullenet, A. Schmitt, and M. Drifford, *J. Phys. Chem.*, **83**, 1924 (1979).

0.05 M aqueous LiCl solvent, the agreement between observation and theory is to within 30%; four of the eight entries agree to within 10%. The theory correctly predicts the observed increase of A_p in the series LiCl, NaCl, and KCl for fixed salt concentration. According to the theory, this behavior is due entirely to differences in equivalent conductances and cation transference numbers of the small-electrolyte solutions in the absence of DNA and has nothing to do with site-specific binding, which is absent from the model.

Rearrangement of the entries in Table IX shows a theoretical decrease of A_p with increasing salt concentration, a trend which is indeterminate from the data.

Comparison with Other Theories

*Theory of Schmitt, Meulenet, and Varoqui.*¹⁵ Schmitt et al. have devised a theory for the electrophoretic mobility of a polyion based on phenomenological quantities called binary, or partial, friction coefficients f_{ij} . We are able to give unique expressions for each of these coefficients involving only the molecular parameters of the present theory. When these expressions are used in the formula of Schmitt et al. for the electrophoretic mobility, the latter reduces to our result. In this sense the two theories are equivalent.

In generating the identities, one must avoid confusing the *signed* electrophoretic mobilities of Schmitt et al. (positive for a cation, negative for an anion) with the mobilities here, which are defined as absolute values. With w for solvent (water), 1 for the counterion, 2 for the co-ion, and 3 for the polyion, we find for the polyion-water, polyion-counterion, and polyion-co-ion friction coefficients, respectively

$$(f_{3w}/L_{Av}) = 3\pi\eta Nb|\ln(\kappa b)|^{-1} \quad (45)$$

$$(f_{31}/L_{Av}) = \frac{1}{3}\nu_1(\nu_1 + \nu_2)^{-1}|z_1||z_2|^{-1}(Q/u_1^s) \quad (46)$$

$$(f_{32}/L_{Av}) = \frac{1}{3}\nu_1(\nu_1 + \nu_2)^{-1}|z_2||z_1|^{-1}(Q/u_2^s) \quad (47)$$

In these formulas, L_{Av} is Avogadro's number; moreover, we recall eq 16 for Q and recall as well that u_i^s is a small-ion electrophoretic mobility in polyelectrolyte-free, small-salt solution.

"Monomer" Theory. Since polymeric electrophoretic mobilities are independent of molecular weight and, moreover, are numerically not very different from electrophoretic mobilities of small charged molecules, formulas like eq 3 were widely used in the older literature and still enjoy some currency. If Q is taken as Nq' , where q' is the structural charge on a monomer, then eq 3 reads

$$300U = q'/\zeta \quad (48)$$

where ζ is now assumed to represent the friction coefficient of the monomer. Such a formula cannot predict the size of the observed ionic-strength dependence of U , and, in fact, as mentioned in connection with the data of Olivera et al., direct measurement of the mobilities of both polymer and monomer do not yield the same result. To the extent that eq 48 does give rough agreement with polyion mobilities, the reason is probably a cancellation of errors. Because of condensation of counterions, use of the structural charge in the numerator is a gross overestimate; and the existence of hydrodynamic interaction among monomers within distance κ^{-1} implies that ζ also grossly overestimates the correct denominator.

*Theories of Overbeek and Stigter*²⁸ and of Hermans.²⁹ The authors used a porous-sphere model to calculate the

electrophoretic mobility of a polyionic chain; the chain is replaced by a uniform distribution of charged beads inside a spherical domain. A Debye-Hückel atmosphere provides a nearly uniform density of counterions within the domain. The charged-solvent effect alone is considered, with the asymmetry field explicitly neglected. Counterion condensation, unknown at the time, is not used to justify the Debye-Hückel approximation (although a direct allusion to the problem involved is made by Overbeek and Stigter at the end of their paper). Hermans' paper is the more frequently cited as being "simple"; but I found Overbeek and Stigter's paper to be just as lucid. The two calculations yield similar results.

As Overbeek and Stigter indicated, the solution of the hydrodynamic problem posed by the model is straightforward. "However, the connection between the model and an actual polyelectrolyte coil is to some extent arbitrary and introduces certain errors." Recognized by the authors as a serious source of error is "the neglect of the microscopic inhomogeneities in the distribution of the countercharge in a polyelectrolyte coil". That is, the countercharge tends to be distributed along the contour of the curvilinear polyion and is not uniformly smeared over the polymeric domain. Among the consequences of this modeling error is that the mobility predicted at high ionic strength is given by the monomer theory, eq 48, with the criterion for "high" being a Debye screening length small compared to the dimension of the polymer domain, a situation nearly always present in practical cases. Thus, the logarithmic dependence on ionic strength characteristic of a linear spatial correlation of polymeric charges is missed. At lower ionic strengths the model is not freely drained, providing some molecular-weight dependence to the mobility. Overbeek and Stigter argue, however, that, on the basis of a more realistic threadlike model (such as the one we employ here), the expected behavior is complete free draining under all conditions of ionic strength (as we predict also).

In fact Overbeek and Stigter made an extraordinarily perceptive comment which contains the seeds of subsequent direction of research in this field. They suggested, in some detail, that the electrophoretic mobility of polyionic chains is probably described more realistically by Henry's theory for charged cylinders than by the porous-sphere theory. It is troubling, therefore, that an influential recent book should have devoted much attention to the latter and none to the former.⁹

Henry's Theory.^{30,31} Henry performed a classical electrohydrodynamic calculation, with explicit neglect of the asymmetry field, resulting in the electrophoretic mobility of an infinitely long cylinder possessing a uniform electric charge on its surface. Averaged over directions parallel and perpendicular to the applied field,³¹ his formula is

$$300U = \epsilon\psi(a)/(6\pi\eta) \quad (49)$$

where $\psi(a)$ is the electrostatic potential at the surface of the cylinder of radius a (the "zeta" potential of classical colloid chemistry). The constant 6π is correct for the limit of small radius relative to Debye length (thickness of "double layer" large compared to radius of curvature of the surface).

If it is assumed that the charge on the surface includes all of the condensed counterions, and if the Debye-Hückel approximation is used for the potential, then, in the limit

(28) J. Th. G. Overbeek and D. Stigter, *Recl. Trav. Chim. Pays-Bas*, **75**, 543 (1956).

(29) J. J. Hermans, *J. Polym. Sci.*, **18**, 527 (1955).

(30) D. C. Henry, *Proc. R. Soc. London, Ser. A*, **133**, 106 (1931).

(31) H. A. Abramson, L. S. Moyer, and M. H. Gorin, "Electrophoresis of Proteins", Reinhold, New York, 1942, Chapter 5.

$\kappa a \rightarrow 0$, eq 49 becomes eq 50. With an exception to be

$$300U = |z_1|^{-1}[\epsilon kT/(3\pi\eta q)]|\ln(\kappa a)| \quad (50)$$

noted, this formula is identical with eq 17, which gives the mobility predicted by our theory if the asymmetry field is not included. The exception is the appearance of a cylindrical radius a in eq 50 in place of the charge spacing b in our result, eq 17. The reason for the difference is the difference in models; Henry used a cylinder of radius a with uniformly smeared surface charge, while we use a line of discrete point charges with uniform spacing b . The numerical difference can be substantial. Although a has no presently well-defined physical meaning for a real polyionic chain, its value chosen to best model DNA is in the range 9–12 Å, while the value of b , which has precise structural meaning, is 1.7 Å.

*Theory of Schellman and Stigter.*³² Rather than using a Debye-Hückel potential with an effective surface charge density given by the prediction of counterion condensation theory, Stigter and Schellman choose a numerical Poisson-Boltzmann potential for $\psi(a)$ in eq 49. They choose that surface charge density which forces agreement of their computed mobility with the measured value. Additionally, they supplement Henry's calculation with an asymmetry field. A negative assessment has been offered for their procedure of forcing agreement between theory and experiment by judicious choice of an adjustable parameter with obscure physical meaning.³³ Indeed, if the natural predictions of theories alternate to ours are not made explicit, there can be no path to objective assessment of relative advantages and deficiencies.

Further Comments on the Present Theory

We discuss here two points concerning the physical origin of the asymmetry field and the apparent implications of the territorial mode of counterion binding¹⁰ for electrophoretic mobilities. It was noted in the Introduction that, contrary to frequent assertion, the asymmetry (relaxation) field does not disappear in a hypothetical small-electrolyte solution with vanishing ionic friction coefficients. The demonstration consists of mere inspection of Onsager's limiting law.³ The asymmetry effect for the polyelectrolyte case is given by the ratio α/β in eq 35. Although eq 38 implies the limiting value unity for β when the small-ionic friction coefficients vanish (infinite small-ionic conductances), the numerator α , given by eq 37, does not reduce to unity in the limit. Indeed, α is identically unity for a symmetrical small electrolyte but in general possesses a constant value not equal to unity.

The physical origin of the term β lies entirely in the relative motion of the polyion and its atmosphere. In the absence of an external field, the polyion is symmetrically enveloped by its atmosphere. Suppose that the field is now turned on and the system reaches its steady state, but suppose also that the polyion is constrained not to move. The symmetry of the atmosphere is destroyed, and the polyion is in general subjected to a net internal electric field. The constraint is now relaxed, and the polyion drifts in the direction determined by the external field. The atmospheric asymmetry is therefore changed by an amount proportional to the drift velocity of the polyion. The departure of β from unity is a measure of this change. If the atmosphere relaxes instantaneously (relative to the drift velocity of the polyion), the change will be vanishingly small. For this reason it is observed from eq 38 that β reduces to unity in the limit $(U^*/\lambda_i^s) \ll 1$. Thus, if one

wished, the *modification* of the asymmetry field caused by the non-zero value of U^*/λ_i^s could be called "the relaxation effect".

The term α reflects a steady-state asymmetry when the polyion is constrained not to move. The counterion and co-ion portions of the atmosphere compete in their effects on the polyion, so the net effect disappears for symmetrical small electrolytes, but in general there is a departure of α from unity independent of ionic mobilities. In summary, the overall asymmetry effect (α/β) is influenced by a relaxation effect ($1/\beta$) that reduces to unity (no effect) for zero small-ionic mobilities.

The mobility-independent part of the asymmetry field is perhaps even more transparent in the "salt-free" case (binary solution consisting of solvent plus electroneutral polyelectrolyte component, with no small electrolyte added).¹³ In ref 13 we used the cylindrical model leading to eq 50 above, but the electrophoretic mobility U for the present model (linear array of discrete charges) under salt-free conditions may be obtained from eq 44 above with λ_p given by eq 15 of ref 13 if a is replaced by b . The analytical structure of U is revealed more clearly by eq 12 of ref 13, where the corresponding values of α and β for the salt-free case are easily identified. We see that α is identically equal to the constant 0.866 and reflects an asymmetrical average positioning of a counterion in the potential energy well centered on the polyion. For a small-electrolyte solution as well, an ion atmosphere may be considered as located within a potential energy well created by the central ion. The equilibrium Boltzmann distribution is then perturbed by an external field in the steady state simply because the potential energy on one side of the central ion becomes less than on the other. Superposed transport effects supplement, but cannot entirely negate, this simple equilibrium phenomenon, no matter how small the friction coefficients of the ions.

There is now the question of how the mode of counterion binding affects the electrophoretic mobility. We recall that at least some, but not necessarily all, bound (condensed) counterions must be territorially bound (i.e., bound to the polyion as a whole, but delocalized).¹¹ Assume first a physical system such that *all* condensed counterions are bound in the territorial mode. Then the charge spacing b is that of the monovalent charged groups built into the covalent structure of the polymer. The charge of the condensed counterions is uniformly distributed among the structural charges, so that the *net* charge on each group is fractional and given explicitly by eq 14. This is the case assumed for all of the numerical work (theoretical values) in Tables I–IX. For most cases considered in the tables, the assumption of all-territorial binding is supported by fairly persuasive experimental evidence.^{2,11,34}

There are two exceptions. The polyion studied by Meulenet et al. (Tables VII and VIII) has a structure which, when more than half neutralized, presents to condensed counterions pairs of closely proximate charged groups. Possibly a subpopulation of condensed counterions is site-bound to this polyion, but the relevant NMR data of the type gathered and cited in ref 34 is lacking. On the other hand, it has been estimated from NMR data that ~15% of the charge of polyphosphate is neutralized by site-bound Li^+ cations.³⁵ If so, the value of b used in eq 35–38 for U should be $2.5 \text{ Å}/0.85 = 2.9 \text{ Å}$ instead of the structural phosphate spacing 2.5 Å used in Table VI. The

(32) J. A. Schellman and D. Stigter, *Biopolymers*, **16**, 1415 (1977).

(33) G. S. Manning, *J. Phys. Chem.*, **82**, 2349 (1978).

(34) J. Reuben, M. Shporer, and E. J. Gabbay, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 245 (1975).

(35) H. S. Kielman, J. M. A. M. van der Hoeven, and J. C. Leyte, *Biophys. Chem.*, **4**, 103 (1976).

theoretical value of $10^4 U$ would then be 1.04, instead of the entry 1.19 in Table VI.

Electrophoretic titrations provide interesting examples of the possibilities. Suppose that a fully neutralized poly(weak acid), such as the one used by Meulenet et al.,²⁷ is titrated with protons. If the metal counterions are territorially bound, then, since all of the protons are site-bound, the appropriate value of b is $b_1 \alpha^{-1}$, where b_1 is the structural charge spacing at full neutralization ($\alpha = 1$). This procedure is the basis of the theoretical correlation of the data in Table VII, where U_{theory} is an increasing function of α . In principle, a similar case should arise when a polyphosphate salt with univalent counterions is titrated by Mg^{2+} , since the latter is presumably site-bound to polyphosphate, at least in the initial titration stage.^{10,36} The prediction, then, is that U decreases as Mg^{2+} is added. Available data are puzzling,³⁷ as the prediction appears to be correct if the univalent counterion is $(\text{CH}_3)_4\text{N}^+$, while, for Na^+ , initial titration with Mg^{2+} does not modify U (see Figure 4 of ref 37). A problem in the interpretation may be the high concentration of 1:1 salt in the solutions. As noted above in connection with the data of Strauss et al.^{25,26} (Table VI), the observed value of U in 0.2 M $(\text{CH}_3)_4\text{N}^+$ is much higher than in the same concentration of Na^+ , contrary to prediction. However, at 0.01 M 1:1 salt, the situation is "normal", the corre-

sponding mobilities being almost the same (see above). It would thus be of interest to have Mg^{2+} titration data at lower salt concentrations.

Consider next a case for which both the univalent cation and the titrating divalent metal cation are territorially bound, a situation that probably arises in DNA solutions, for example.² The value of b for the model remains fixed at the structural value throughout the titration. The initial version of counterion condensation theory for mixed uni-divalent counterion systems³⁸ would predict an initially invariant polyion charge with consequent invariance of the mobility, but the predictions of current theory² are more complex. Figure 5 of ref 2 shows that the net polyion charge decreases monotonically as more divalent cations are territorially bound; invariant-charge behavior is the limiting envelope as the ionic strength tends to zero. Therefore the prediction again is that U decreases as titration proceeds, a qualitative behavior which has been observed,³⁹ although the data are perhaps not clear-cut, the $(\text{CH}_3)_4\text{N}^+$ univalent cation employed having since been found to interact specifically with DNA.^{22,23}

It is conceivable that territorially bound and site-bound titrating ions may be distinguished on a quantitative level by the distinct theoretical calculations employed to model them.

(36) P. Spegt and G. Weill, *Biophys. Chem.*, **4**, 143 (1976).

(37) U. P. Strauss and A. Siegel, *J. Phys. Chem.*, **67**, 2683 (1963).

(38) G. S. Manning in "Polyelectrolytes", E. S  l  gny, Ed., Reidel, Dordrecht, Holland, 1974.

(39) P. D. Ross and R. L. Scruggs, *Biopolymers*, **2**, 79 (1964).

Crossed Molecular Beam Studies of Proton Transfer, Unimolecular Decay, and Isotope Scrambling in the Reactions $\text{H}_2^+ + \text{H}_2\text{O}$, $\text{H}_2^+ + \text{D}_2\text{O}$, and $\text{D}_2^+ + \text{H}_2\text{O}$

R. M. Bilotta and J. M. Farrar*

Department of Chemistry, University of Rochester, Rochester, New York 14627 (Received: December 1, 1980)

We present an experimental study of the title reactions over the collision energy range from 0.7 to 6.9 eV. Over the entire collision energy range, a significant fraction of the products have internal excitation sufficiently high to undergo unimolecular decay to H_2O^+ or an isotopically substituted water cation. An examination of the reactions $\text{D}_2^+ + \text{H}_2\text{O}$ and $\text{H}_2^+ + \text{D}_2\text{O}$ and observation of H_2O^+ and HOD^+ products of unimolecular decay at 3.0 and 6.3 eV suggest that, at the lower collision energy, the recoil energy distributions are consistent with the results of phase space calculations including all vibrations of the H_2O^+ or HOD^+ product. At this collision energy, the unimolecular decay products have barycentric angular distributions with sharp forward-backward symmetry, suggesting that planar scattering with concomitant angular momentum polarization is an important dynamical feature in these reactions. At the higher collision energy, the complex "osculates" with a lifetime too short for rapid intramolecular energy transfer. We also present evidence for a direct reaction between H_2^+ and D_2O yielding HOD^+ and a bound HD molecule, proceeding through a four-center exchange reaction rather than through unimolecular decay of HD_2O^+ .

Introduction

The study of ion-neutral reaction dynamics in the gas phase has experienced significant growth in recent years through the impetus of experimental and theoretical advances allowing ionic systems to be studied in increasing detail.¹ One of the ultimate goals of these studies is the elucidation of the dynamics of ion-neutral interactions in the single collision regime. The development of instru-

mentation for studying such interactions at low collision energies as well as theoretical techniques for computing potential surfaces and the dynamics of systems on these surfaces has begun to make this goal a realizable one.

Within the broad category of ion-neutral interactions, proton transfer reactions are of special interest because of their intrinsic chemical simplicity and their pervasiveness in a wide variety of processes.² The realization that

(1) See, for example, M. T. Bowers, Ed., *Gas Phase Ion Chem.*, **1**, 2 (1979).

(2) R. W. Taft in "Kinetics of Ion-Molecule Reactions", P. Ausloos, Ed., Plenum Press, New York, 1979, p 271.