Theory of the Polyion Diffusion Constant in Polyelectrolyte Solutions Containing Low Molar Mass Electrolyte

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ABSTRACT: The purpose of the paper is to investigate the influence of the strong polyion–counterion interactions on the diffusion of polyions in a polyelectrolyte solution of low macromolecular concentration containing additional low molar mass electrolyte. The thermodynamic theory has been established without use of a force-balance equation for the polyion in order to avoid problems related to the average force due to electrostatic interactions acting on the highly charged, large polyions. Instead the hydrodynamic force acting on the polyion under stationary conditions is used to establish the relation between polyion velocity and polyion concentration gradient. A cell model has been applied: in this model a cubic cell of volume C_P^{-1} (C_P being the concentration of polyions per unit volume) containing one polyion, small ions, and solvent and surrounded by the other macroscopic domain is assumed to be electroneutral and to migrate together with its central polyion. The cell boundaries are permeable to solvent molecules and small ions only. Within the cell volume the solvent velocity relative to the polyion is obtained from the Navier–Stokes equation, which leads to an expression for the hydrodynamic force on the polyion. For the small ions force-balance equations are established involving the diffusion potential. An important feature of the cell model used is that the activity and the velocity (or flux) of the low molar mass particles are the only quantities which are assumed to be continuous on the boundaries between the microscopic cell and its macroscopic surroundings. The final result shows that the diffusion constant of the polyion is strongly influenced by the activity coefficient γ_P of the counterions (in the sense of the additivity rule for the counterion activity). In the presence of an excess of low molar mass electrolyte the diffusion constant of the polyions will increase with C_P and decrease with the electrolyte concentration.

1. Introduction

The diffusion constant, D_P, is an important quantity characterizing the translational dynamics of polyions and is related to concentration fluctuations in polyelectrolyte solutions.[1,2] For ideal Brownian particles the diffusion constant depends in a simple way, through the Einstein relation, on the friction coefficient of the particles in the given solvent. In more complicated systems where particles strongly interact, such as in polymer solutions in the semidilute regime, the diffusion constant exhibits an important concentration dependence[3-6] that has not yet been completely clarified. Another case of nonideal diffusion arises in even fairly dilute polyelectrolyte solutions and is due to charge effects. Diffusion in a system of charged particles is always accompanied by a diffusion potential which arises macroscopically from the concentration gradients in the solution. This diffusion potential must play an important role in the statistical mechanical treatment of the diffusion process. It is thought to make an essential contribution in the Langevin equation for the polyions as it must affect the random force contribution. Although some theoretical approaches to the diffusion constant of polyelectrolyte solutions based on the Langevin equation have been made,[7-10] it still remains a difficult and unsolved problem.

But even from the thermodynamic point of view the charge effects in polyion diffusion have not yet been well clarified.[11-13] Three charge effects may be distinguished. The first arises from electrostatic interactions between the polyions and is related to concentration effects as observed in solutions of ordinary polymers but with specific electrostatic problems. It may be thought to vanish at infinite dilution or very high concentrations of low molar mass electrolyte. A second effect, without any equivalence for uncharged macromolecules, cannot be diminished under the same circumstances, since it arises from the interaction between a polyion and the small ions in solution. Under the effect of a polyion concentration gradient, polyions and their counterions both migrate in the direction of lower concentration. As the counterions have a much smaller friction coefficient than the polyions, they will have a tendency to move faster, thus accelerating the diffusion velocity of the polyions through the strong attractive force exercised on the counterions, which is also affected by the presence of coions. It is therefore obvious that the diffusion of the polyion may depend on the friction constant of the low molar mass ions. The same effect is also responsible for the diffusion potential. There is a third effect due to charge interactions which arises from the distortion of the small ion distribution around each polyion under the influence of the concentration gradient of the polyions. It has been generally assumed to be less significant and therefore neglected in spite of its importance.

It remains at present still difficult to derive a complete theory of polyion diffusion taking into account the three charge effects mentioned above, which, probably, are not independent of each other at finite dilution. The main problem is related to the derivation of an expression for the average force acting on a given polyion in the nonequilibrium situation and arising from all the charged particles present. It is, in this respect, important to note that a mean electric potential ψ derived from a Poisson equation for the system of polyions and small ions (as is the case for the diffusion potential) *cannot* be regarded as the potential of the mean force acting on the polyion. This is even true for polyelectrolyte solutions at finite dilution, where contributions to ψ from more than one polyion may be neglected. There are at least two reasons the average force on a polyion carrying n elementary charges e_0 cannot simply be represented by $-ne_0\vec{\nabla}\psi$. The first is that due to the distribution of the polyion charges over a region of space of nonnegligible size, the value of $-\vec{\nabla}\psi$ for the polyion cannot be established unambiguously with respect to that for the small ions; it would be possible to do so for the individual charged sites on the polyion, however. The second derives from the fact that for $-\vec{\nabla}\psi$

0024-9297/82/2215-1562$01.25/0

to represent the average force acting on a charged particle, the local value of ψ should only be slightly affected by the removal or the introduction of that particle itself. This, although true if a small ion carrying only a few elementary charges is considered, cannot be assumed to hold for a large and highly charged polyion. Therefore, contrary to what is usually done in the treatment of diffusion problems for systems containing small ions only and where the interactions are taken into account in the force-balance equations for the different kind of particles through the average diffusion potential,[11,12] for the case of polyelectrolyte solutions such a procedure should be avoided insofar as the polyion itself is considered.

In this paper we derive an expression for the polyion diffusion constant in a low molar mass electrolyte containing polyelectrolyte solution using a cell model approach. Polyion–polyion interactions will be neglected, limiting the validity of the treatment to dilute solutions. No force-balance equation for the polyion is directly derived but the hydrodynamic force acting on the polyion under stationary conditions will be used to establish the relation between polyion velocity and polyion concentration gradient. For that purpose the solvent velocity relative to the polyion inside the cell, assumed to remain electroneutral, will be expressed, starting from the Navier–Stokes equation.

We limit our problem to that of a natural diffusion process of polyions where no macroscopic electric current exists. We therefore do not consider particular experimental conditions under which the diffusion potential is a priori fixed, for instance, conditions that lead to $\psi_D = 0$; the diffusion constant under such conditions must be different from that considered here. Note that the absence of a macroscopic electric force arising from the diffusion potential has sometimes been used in treatments based on the Langevin equation.

2. Model and Fundamental Equations

Consider a polyion solution at rest with respect to an external rectangular coordinate system X,Y,Z and with a positive concentration gradient of the polyions in the X direction, $\vec{\nabla} C_P = (\partial C_P/\partial X)\vec{1}_X$. Here, the polyion concentration $C_P = C_P(X)$ is expressed in number of particles per unit volume. Under the influence of the concentration gradient the polyions diffuse in the X direction with a *stationary* velocity $\vec{U}_P = -U_P(X)\vec{1}_X$. The diffusion coefficient D_P may be defined according to Fick's first law by

$$D_P = U_P/(\partial \ln C_P/\partial X) \qquad (2.1)$$

The polyion concentration C_P is chosen small enough to allow for the neglect of polyion–polyion interactions.

Focusing our attention on a given polyion, we assume it to have its center of mass at the center of a cubic cell with side length L and volume V_P equal to the average free volume per macromolecule, $V_P = C_P^{-1}$. One of the edges of this cell is parallel to the X axis and we shall not take into consideration any rotation of this volume element in the course of the diffusion process. We further assume that this cell contains only *one* polyion and its counterions besides the solvent and additional low molar mass electrolyte and that it is *electroneutral*. It will migrate with the same velocity as its central polyion without violating the above assumptions at any moment, although V_P will gradually increase in the course of the diffusion process due to the decrease of the average polyion concentration in the diffusion direction. We finally assume that by treating the interior of the cell on a more microscopic basis than the rest of the solution, the features of the macroscopic diffusion process are not affected.

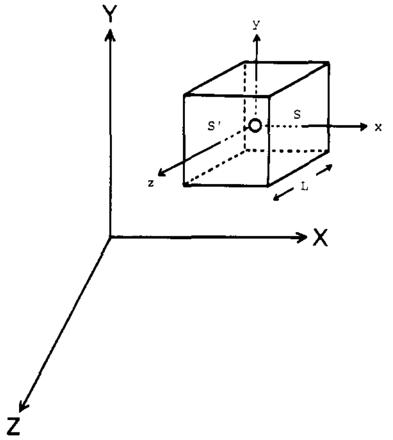

Figure 1. Cell model and the coordinate systems used.

Let us now adopt a rectangular coordinate system x,y,z that has its origin fixed at the center of the cell and the three axes oriented parallelly to the three adjoining edges of the cube such that $\vec{1}_x = \vec{1}_X$ (see Figure 1). Positions in this coordinate system are expressed relative to that of the moving polyion. We define $f_i(x,y,z)$ and $\nu(x,y,z)$ as the microscopic number concentration of the low molar mass ions of species i in V_P and the spatial density of polyion segments, respectively. The latter is assumed to remain unperturbed in the course of the diffusion. The small ions will move with a velocity $\vec{v}_i(x,y,z)$ relative to the central polyion. The components of the velocities $\vec{v}_i$ obey the following boundary conditions in our model:

$$v_{i,y} = 0 \text{ on the } xz \text{ plane at } y = -L/2 \text{ and } y = \tfrac{1}{2} \qquad (2.2a)$$

$$v_{i,z} = 0 \text{ on the } xy \text{ plane at } z = -L/2 \text{ and } z = L/2 \qquad (2.2b)$$

expressing that no net flow of counterions in a direction different from $\vec{1}_x = \vec{1}_X$ occurs.

Our first aim is to obtain the hydrodynamic force acting on the central polyion in the stationary state. For this purpose let us imagine that the polyion and its free volume V_P are at rest but the solvent flows relative to the polyion with a stationary velocity $\vec{u}_w = u_w(x)\vec{1}_x$ in the x direction. This velocity must obey the following Navier–Stokes equation within V_P:

$$\eta\nabla^2 u_w - \frac{\partial}{\partial x}(P - kT\sum_i f_i) - \sum_i \xi_i f_i(u_w - v_{i,x}) - \xi_0 u_w \nu = 0 \qquad (2.3)$$

Here ∇^2 is the Laplacian with respect to x,y,z and η, P, ξ_i, and ξ_0 are the solvent viscosity, the hydrodynamic pressure, the friction constant of ion species i, and the friction constant of a polyion segment, respectively. In the second term on the left-hand side of (2.3) appears the local osmotic pressure due to the distributed small ions, $kT\sum_i f_i$. The third and the fourth terms are friction forces per unit volume of the solvent against the distributed small ions and against the polyion segments. The factor $u_w - v_{i,x}$ is the solvent velocity in the x direction relative to the ions of species i.

Integration of (2.3) over V_P with the additional condition $\partial u_w/\partial x = 0$ at $x = -L/2$ and $x = L/2$ (i.e., on the planes S' and S, respectively; see Figure 1), a condition following from the incompressibility of the solvent, leads to

$$-L^2\Delta\langle P\rangle_S + L^2 kT\sum_i \Delta\langle f_i\rangle_S + \int^{V_P}\sum_i \xi_i f_i(v_{i,x} - u_w)\,\mathrm{d}V - \xi_0\int^{V_P} u_w\nu\,\mathrm{d}V = 0 \qquad (2.4)$$

Here, the difference between the average value of q (standing for either the hydrodynamic pressure P or the concentration f_i of ions i) over the yz plane S at $x = L/2$ and S' at $x = -L/2$ is defined by

$$\Delta\langle q\rangle_S \equiv \frac{1}{L^2}\left(\int^S q\ \mathrm{d}y\ \mathrm{d}z - \int^{S'} q\ \mathrm{d}y\ \mathrm{d}z\right) \quad (2.5)$$

The third term on the left-hand side of (2.4) can be transformed with the help of the continuity equation for the small ions within the volume element considered. For each species i we have

$$\partial f_i/\partial t + \vec{\nabla}\cdot f_i\vec{v}_i = 0 \quad (2.6)$$

where $\partial/\partial t$ stands for differentiation with respect to time at constant x,y,z. Even in a steady-state polyion diffusion, $\partial f_i/\partial t$ will be nonvanishing since the value of V_P steadily increases in the course of the diffusion process. This contribution is negligible, however, when U_P is sufficiently small as it is of order $U_P{}^2$.

$$\frac{\partial f_i}{\partial t} = -\frac{\partial f_i}{\partial V_P}\frac{\partial V_P}{\partial X}U_P = \frac{\partial f_i}{\partial V_P}\left(\frac{1}{C_P}\frac{\partial \ln C_P}{\partial X}\right)U_P = -\left(\frac{\partial f_i}{\partial V_P}\right)\frac{V_P}{D_P}U_P{}^2 \quad (2.7)$$

Here, use has been made of (2.1) and of the definitions $V_P = C_P{}^{-1}$ and $\partial X/\partial t = -U_P$. Thus the first term on the left-hand side of (2.6) may be neglected in first order for the steady-state polyion diffusion.

Integration of (2.6) over the total free volume V_P gives under these conditions the following efflux–influx balance equation for the small ions of species i:

$$\int^S f_i v_{i,x}\ \mathrm{d}y\ \mathrm{d}z - \int^{S'} f_i v_{i,x}\ \mathrm{d}y\ \mathrm{d}z = 0$$

or

$$\langle f_i v_{i,x}\rangle_S = \langle f_i v_{i,x}\rangle_{S'} \quad (2.8)$$

On the other hand, the following relation is obtained from (2.6) without the $\partial f_i/\partial t$ term:

$$\vec{\nabla}\cdot x f_i\vec{v}_i = f_i v_{i,x} \quad (2.9)$$

which, after integration over V_P, taking into account the boundary conditions (2.2) and the balance equation (2.8), yields

$$V_P\langle f_i v_{i,x}\rangle_S = \int^{V_P} f_i v_{i,x}\ \mathrm{d}V \quad (2.10)$$

This last equation may be used to express the total friction force arising from the small ions in volume V_P

$$\sum_i \int^{V_P} \xi_i f_i(v_{i,x} - u_w)\ \mathrm{d}V = V_P\sum_i \xi_i\langle f_i(v_{i,x} - u_w)\rangle_S - \sum_i \int^{V_P} \xi_i\{f_i u_w - \langle f_i u_w\rangle_S\}\ \mathrm{d}V \quad (2.11)$$

Substituting (2.11) into (2.4) we obtain the following force-balance equation within the free volume element:

$$L^2\Delta\langle P\rangle_S + \int^{V_P}(\xi_0\nu u_w + \sum_i \xi_i\{f_i u_w - \langle f_i u_w\rangle_S\})\ \mathrm{d}V = L^2kT\sum_i \Delta\langle f_i\rangle_S + V_P\sum_i \xi_i\langle f_i(v_{i,x} - u_w)\rangle_S \quad (2.12)$$

This force-balance equation can be used to relate the polyion concentration gradient to the polyion velocity, provided suitable continuity conditions on the surface of the free volume element can be formulated. This will be done in the next section.

The electric current per unit area I passing through the surface S in the x direction can be expressed by

$$I = \sum_i z_i e_0\langle f_i v_{i,x}\rangle_S \quad (2.13)$$

where z is the valency of ions of species i and e_0 the elementary charge. This current density I can be regarded as the macroscopically observable current density in the X direction at the position of S, since the motion of the volume element itself cannot contribute to the electric current in view of its electroneutrality. In the case of steady-state diffusion $I = 0$ so that (2.13) provides an additonal relation for solving the diffusion equation.

Hereafter, for simplicity, we restrict ourselves to the case of a solution containing only two species of low molecular weight ions, namely, univalent cations and univalent anions, and a polyion with a segmental charge $+e_0$. For this case (2.12) and (2.13) take the following form:

$$L^2\Delta\langle P\rangle_S + \int^{V_P}(\xi_0\nu u_w + \xi_+\{f_+u_w - \langle f_+u_w\rangle_S\} + \xi_-\{f_i u_w - \langle f_i u_w\rangle_S\})\ \mathrm{d}V = L^2kT(\Delta\langle f_+\rangle_S + \Delta\langle f_-\rangle_S) + V_P(\xi_+\langle f_+(v_+ - u_w)\rangle_S + \xi_-\langle f_-(v_- - u_w)\rangle_S) \quad (2.14)$$

$$\langle f_+v_+\rangle_S - \langle f_-v_-\rangle_S = 0 \quad (2.15)$$

Here, the subscript x under v_+ and v_-, denoting the component in the x direction, has been omitted for simplicity.

3. Continuity Conditions on the Cell Boundaries

On the yz plane (S) of the cell boundary some microscopically defined quantities should be analytically connected with quantities defined in the outer macroscopic domain. First, it is reasonable to assume that $\langle f_i\rangle_S$ is identical with the macroscopically observable activity a_i of the ions of species i at the position X of S. Therefore

$$\langle f_i\rangle_S = a_i(X) \quad (3.1a)$$

$$\Delta\langle f_i\rangle_S = (\partial a_i/\partial X)L \quad (3.1b)$$

Second, since there is no net flow of the solvent, the following relation should be obeyed, connecting the solvent flow through S to the polyion velocity:

$$\langle u_w\rangle_S = U_P \quad (3.2)$$

Next, if we define by V_+ and V_- the absolute velocities of the positive and negative small ions in the X direction within the macroscopic solutions, respectively, the velocities of these species relative to that of the polyion are given by $V_+ + U_P$ and $V_- + U_P$, respectively. These velocities should be continuously connected to the microscopic velocities on S such that

$$\langle v_+\rangle_S = V_+ + U_P \quad (3.3a)$$

$$\langle v_-\rangle_S = V_- + U_P \quad (3.3b)$$

It should be noted that only eq 3.1 to 3.3 are thought to be physically rational conditions, ensuring continuity between the cell and the outside macroscopic domain. It cannot be excluded that other quantities are discontinuously connected between the two regions. For example, the electric field or the gradient of the chemical potential of the small ions may not always be continuous.

The hydrodynamic pressure $\langle P\rangle_S$ in eq 2.12 or 2.14 can be interpreted as the pressure balancing the osmotic pressure on $S(X)$ arising from the polyion at the position X since the boundaries of the cell act as semipermeable membranes being impermeable against polyions but completely permeable for solvent molecules and low molar mass ions. Therefore

$$L^2\Delta\langle P\rangle_S = -L^2\{\tilde{\Pi}(S) - \tilde{\Pi}(S')\} = -L^2\left(\frac{\partial\tilde{\Pi}}{\partial X}\right)L = -\frac{\partial \ln C_{\mathrm{P}}}{\partial X}\left(\frac{\partial\tilde{\Pi}}{\partial C_{\mathrm{P}}}\right) \quad (3.4)$$

where $\tilde{\Pi}$ denotes the osmotic pressure due to polyions only in a bulk polyelectrolyte solution at equilibrium. If the polyions would behave as ideal solutes, $\tilde{\Pi}$ would be given by $\tilde{\Pi} = C_{\mathrm{P}}kT$. This is, however, not the case and therefore it is more realistic to put

$$\partial\tilde{\Pi}/\partial C_{\mathrm{P}} = \phi_{\mathrm{P}}kT \quad (3.5)$$

where ϕ_{P} (<1) is related to the osmotic coefficient and dependent on C_{P}, the polyion charge ne_0, and the concentration C_s of low molar mass electrolyte. This coefficient should tend to unity in an extremely diluted polyion solution ($V_{\mathrm{P}} \rightarrow V$) and approach zero for a completely ordered structure as may appear at very high concentrations.

Finally, we can express the total hydrodynamic force on the polyion segments, appearing in (2.12) or (2.14), as a force proportional to the polyion velocity with a friction constant ξ_{P} defined by

$$\xi_{\mathrm{P}}U_{\mathrm{P}} \equiv \xi_0\int^{V_{\mathrm{P}}} u_w\nu \,\mathrm{d}V \quad (3.6)$$

Analogously we can define a friction constant ξ_c through the relation

$$\xi_c U_{\mathrm{P}} \equiv \sum_i \xi_i \int^{V_{\mathrm{P}}} \{f_i u_w - \langle f_i u_w\rangle_S\}\,\mathrm{d}V \quad (3.7)$$

This force is related to the hydrodynamic force on the small ions if they would move with same velocity as the polyion, corrected for its value on the surface of the free volume element.

After substitution into (2.14) of (3.1) and (3.4) to (3.7) and use of the condition (2.15), the following equation is obtained:

$$\phi_{\mathrm{P}}kT\frac{\partial \ln C_{\mathrm{P}}}{\partial X} = -(\xi_{\mathrm{P}} + \xi_c)U_{\mathrm{P}} + V_{\mathrm{P}}kT\frac{\partial(a_+ + a_-)}{\partial X} + V_{\mathrm{P}}(\xi_+\langle f_+(v_+ - u_w)\rangle_S + \xi_-\langle f_-(v_- - u_w)\rangle_S) \quad (3.8)$$

This equation still contains the microscopic factor $\langle f_i(v_{i,x} - u_w)\rangle_S$, which can, however, be related to the macroscopic velocities $V_{i,X}$ if the additional assumption is made that f_i and the velocities of ions i on the surface S are only weakly correlated.

$$\langle f_i(v_{i,x} - u_w)\rangle_S \simeq \langle f_i\rangle_S\langle v_{i,x} - u_w\rangle_S = a_iV_{i,x} \quad (3.9)$$

Here, (3.1), (3.2), and (3.3) have been used. With (3.8) and (3.9) we obtain the relation between $\partial \ln C_{\mathrm{P}}/\partial X$, U_{P}, V_+, and V_- in terms of macroscopic quantities only.

$$-\phi_{\mathrm{P}}kT\frac{\partial \ln C_{\mathrm{P}}}{\partial X} = -(\xi_{\mathrm{P}} + \xi_c)U_{\mathrm{P}} + C_{\mathrm{P}}^{-1}kT\frac{\partial \ln (a_+ + a_-)}{\partial X} - C_{\mathrm{P}}^{-1}(\xi_+a_+V_+ + \xi_-a_-V_-) \quad (3.10)$$

From this last relation V_+ and V_- can be eliminated by expressing them as a function of the polyion velocity and the activity of the small ions. This will be done in the next section, where explicit expressions for D_{P} will be derived.

4. Expression for the Diffusion Coefficient D_{P} and Discussion

In the force-balance equation for the polyion the use of the diffusion potential ψ_{D} has been avoided by the model outlined in the preceding sections. In order to derive expressions for the diffusion coefficient of the polyion not containing V_+ and V_- explicitly, these quantities may be eliminated through the macroscopic force-balance equations for the small ions in which the diffusion potential may appear as mentioned in the Introduction. They have the following form:

$$\xi_+a_+V_+ + kT\frac{\partial a_+}{\partial X} + a_+e_0\frac{\partial\psi_D}{\partial X} = 0 \quad (4.1\mathrm{a})$$

$$\xi_-a_-V_- + kT\frac{\partial a_-}{\partial X} - a_-e_0\frac{\partial\psi_D}{\partial X} = 0 \quad (4.1\mathrm{b})$$

From (4.1) and the condition for zero current in the approximation consistent with (3.9), i.e.

$$a_+V_+ = a_-V_- + (a_- - a_+)U_{\mathrm{P}} \quad (4.2)$$

the following expressions may be derived for V_+ and V_-, respectively:

$$a_+V_+ = -\frac{a_+\xi_-(a_+ - a_-)}{(a_-\xi_+ + a_+\xi_-)}U_{\mathrm{P}} - \frac{kT}{(a_-\xi_+ + a_+\xi_-)}\frac{\partial a_+a_-}{\partial X} \quad (4.3\mathrm{a})$$

$$a_-V_- = +\frac{a_-\xi_+(a_+ - a_-)}{(a_-\xi_+ + a_+\xi_-)}U_{\mathrm{P}} - \frac{kT}{(a_-\xi_+ + a_+\xi_-)}\frac{\partial a_+a_-}{\partial X} \quad (4.3\mathrm{b})$$

Substituting (4.3) into (3.19) and expressing differentiation with respect to X in the following way

$$\partial/\partial X = C_{\mathrm{P}}(\partial \ln C_{\mathrm{P}}/\partial X)(\partial/\partial C_{\mathrm{P}}) \quad (4.4)$$

we obtain after some rearrangements the fundamental equation for the diffusion coefficient, using (2.1) and the definition of V_{P}

$$D_{\mathrm{P}}/kT = \{\phi_{\mathrm{P}} + (a_- - a_+)\{\xi_+(\partial a_-/\partial C_{\mathrm{P}}) - \xi_-(\partial a_+/\partial C_{\mathrm{P}})\}(a_-\xi_+ + a_+\xi_-)^{-1}\}/\{(\xi_{\mathrm{P}} + \xi_c) + \xi_+\xi_-(a_- - a_+)^2C_{\mathrm{P}}^{-1}(a_-\xi_+ + a_+\xi_-)^{-1}\} \quad (4.5)$$

The general equation (4.5) may somewhat be simplified by applying the assumption that, the friction constants of small, univalent ions being of approximately the same value (with the evident exception of H^+ or OH^-), they may in a first approximation be replaced by an average value $\xi_\pm$

$$\xi_+ \simeq \xi_- \simeq \xi_\pm \quad (4.6)$$

In this approximation the diffusion coefficient (D_{P}) is given by

$$\frac{D_{\mathrm{P}}}{kT} = \frac{\phi_{\mathrm{P}} + (a_- - a_+)(\partial a_-/\partial C_{\mathrm{P}} - \partial a_+/\partial C_{\mathrm{P}})(a_- + a_+)^{-1}}{(\xi_{\mathrm{P}} + \xi_c) + \xi_\pm(a_- - a_+)^2C_{\mathrm{P}}^{-1}(a_- + a_+)^{-1}} \quad (4.7)$$

Both in (4.5) and in (4.6) the activities of the counterions and the coions, i.e., a_- and a_+, respectively, depend on the local concentrations of polyions and salt. If the polyion velocity $-U_{\mathrm{P}}$ is sufficiently small, equilibrium relations for these dependences may be used in a first approximation, as the error will or order U_{P}^2. These equilibrium relations are not well established yet although several approximate expressions have been proposed. In order to obtain a first impression about the C_{P} and C_s dependences of D_{P}, we may use the most simple approach which corresponds to the experimentally more or less satisfied "additivity rule".

$$a_- \simeq \gamma_{\mathrm{P}}nC_{\mathrm{P}} + C_s \quad (4.8\mathrm{a})$$

$$a_+ \simeq C_s \quad (4.8\mathrm{b})$$

Here, the coefficient γ_{P} is the activity coefficient of the counterions in a salt-free solution of the same polyion concentration C_P, each polyion carrying n elementary positive charges. It is independent of C_s and has been found not to depend appreciably on C_P for dilute polyelectrolyte solutions with a value around 0.2–0.3, so that $\partial\gamma_P/\partial C_P$ may be put approximately equal to zero. Substituting (4.8) into (4.5) we obtain the following simple C_P and C_s dependences for D_P:

$$\frac{D_P}{kT} = \frac{\phi_P + \xi_+ n\gamma_P{}^2 C_P\{(\xi_+ + \xi_-)C_s + \xi_+ n\gamma_P C_P\}^{-1}}{(\xi_P + \xi_c) + \xi_+\xi_- n^2\gamma_P{}^2 C_P\{(\xi_+ + \xi_-)C_s + \xi_+ n\gamma_P C_P\}^{-1}} \tag{4.9}$$

$$\simeq \frac{\phi_P + n\gamma_P{}^2 C_P(2C_s + n\gamma_P C_P)^{-1}}{(\xi_P + \xi_c) + \xi_\pm n^2\gamma_P{}^2 C_P(2C_s + n\gamma_P C_P)^{-1}} = \frac{D_P'}{kT}$$

These expressions clearly demonstrate that for $C_P/C_s \rightarrow 0$, the diffusion coefficient obeys the simple relation (as $\phi_P \rightarrow 1$ under these conditions)

$$\lim_{C_P/C_s \rightarrow 0} (D_P/kT) = (\xi_P + \xi_c)^{-1} \tag{4.10}$$

A comparison of (3.6) with (3.7) shows that it will be difficult in general to predict how ξ_c compares to ξ_P although we guess $\xi_i < \xi_0$. Only if under certain given conditions ξ_c is negligible with respect to ξ_P would (4.10) reduce to the Einstein relation. In general, however, for $C_P/C_s \rightarrow 0$ the polyion diffusion coefficient D_P will be smaller than the prediction by this relation.

An important conclusion is that in the presence of an excess of salt ($nC_P \ll C_s$) the diffusion coefficient of the polyion will increase above its value at infinite dilution with both C_P and n, dependent, however, on the value of C_s. The effect of the low molar mass electrolyte always appears through the ratio $n\gamma_P C_P/C_s$. No experimental evidence for these effects is available yet due to the scarcity of systematic experimental data. Qualitatively it has been found that D_P has a tendency to increase with polyion charge and to decrease with salt concentration.

In the expression for D_P the factor ϕ_P may be assumed to be close to unity only for very dilute solutions. It remains an additional problem to derive an explicit expression for the C_P, C_s, and n dependence of ϕ_P, which is related to the virial coefficients of the polyions in the polyelectrolyte–electrolyte solution.

Our eq 4.9 may be compared to the expressions for D_P derived from nonequilibrium thermodynamics by Varoqui and Schmitt[13] and from a molecular theory by Eisenberg.[2] In both theories the force on the polyion is expressed through the gradient of a local average electrostatic potential, a procedure that raises some questions as pointed out in section 1. In the former an expression for D_P is derived that is analogous to (4.10) in the limit $C_P \rightarrow 0$. Our treatment gives an explicit dependence of D_P on C_P, n, and C_s, which is missing in the expression derived by Varoqui and Schmitt. It should be remembered, however, that our treatment is only applicable as long as polyion–polyion interactions may be neglected in a first approximation.

In Eisenberg's theory a charge shielding parameter i is introduced a priori in order to express the electric force acting on the polyion through an *effective charge.* Such an effective charge n^*e may be defined through the relation

$$n^* = \gamma_P n \tag{4.11}$$

which is consistent with the additivity rule. Our derivation, which can avoid the problem of the averaged electric force on the polyion altogether, shows, however, that D_P cannot be expressed as a function of n^* only, due to the factor $n\gamma_P{}^2 = \gamma_P n^* = n^{*2}/\gamma_P$, which appears both in the numerator and in the demoninator of (4.9). This makes the direct comparison between Eisenberg's expression and (4.9) rather difficult.

Finally, it should be noted that the same model as used here can be applied to the problem of electrophoresis using suitable boundary conditions ($\partial a_\pm/\partial X = 0$, $\Delta\langle P\rangle_S = 0$, $\Delta\langle f_i\rangle_S = 0$) and replacing $\partial\psi_D/\partial X$ in (4.1) by the applied electric potential gradient. Of course, the condition of zero current (eq 4.2) has to be omitted in this case. We shall not consider this problem in the present paper, however.

Acknowledgment. M.M. gratefully acknowledges financial support by the Japan Society for the Promotion of Science (JSPS) through a fellowship for research in Japan. It was during his stay in Japan (1980) that the present work was initiated.

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