CALCULATION OF THE ELECTROPHORETIC MOBILITY OF A PARTICLE BEARING BOUND POLYELECTROLYTE USING THE NONLINEAR POISSON-BOLTZMANN EQUATION

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ABSTRACT A numerical method for determining the electrophoretic mobility of a polyelectrolyte-coated particle is presented. The particle surface is modeled as having a permeable layer of polyelectrolyte molecules anchored to its surface. Fluid flow within the polyelectrolyte layer is subject to Stokes drag arising from the polyelectrolyte segments. The method allows arbitrary distribution of polymer segments and charge density normal to the surface to be used. The hydrodynamic plane of shear may also be varied. The potential profile is determined by a numerical solution to the nonlinearized Poisson-Boltzmann equation. The potential profile is then used in a numerical solution to the Navier-Stokes equation to give the required mobility. The use of the nonlinearized Poisson-Boltzmann equation extends the results to higher charge density/lower ionic strength conditions than previous treatments. The surface potentials and mobilities for three limiting charge distributions are compared for both the linear and nonlinear treatments to delimit the range of validity of the linear treatment. The utility of the numerical, nonlinear treatment is demonstrated by an improved fit to the electrophoretic mobility of human erythrocytes as a function of ionic strength in the range 10 to 150 mM.

INTRODUCTION

It has long been recognized that classical theories of electrophoresis usually overestimate the mobilities of particles such as erythrocytes that bear polymers or polyelectrolyte on their surfaces. Three similar approaches that more successfully treat such cases by taking into account the fluid drag of the polymeric surface phase have been published recently (Donath and Pastushenko, 1980; Wunderlich, 1981; Levine et al., 1983). In each case the linearized Poisson-Boltzmann equation was used, i.e., the potential everywhere was assumed to be $<kT/e$. For typical charge densities encountered with cells and biological material, this limits the applicability of these results to ionic strengths >20 mM. Moreover since the required mobility is obtained by integration of the Navier-Stokes equation, which contains a charge density term, the validity of the linearized Poisson-Boltzmann equation may be even more restricted.

To deal with this problem the treatment of Levine et al. (1983) has been extended using the full nonlinear Poisson-Boltzmann equation. This necessitated the use of numerical methods to solve both the Poisson-Boltzmann and Navier-Stokes equations. A further advantage of the numerical approach is that it allows the use of arbitrary distributions of charge and fluid drag components in the direction normal to the particle surface. The three previous treatments assumed that the frictional components were uniformly distributed for mathematical convenience. The charge distributions were either very simple (Levine et al., 1983) or were represented in the final expressions by integrals that were inconvenient to evaluate (Donath and Pastushenko, 1980; Wunderlich, 1981). In addition, with the numerical approach the position of the hydrodynamic shear plane can easily be varied. We report here a general method for calculating the electrophoretic mobility of any large particle bearing adsorbed or covalently bound polymer or polyelectrolyte on its surface, valid for any charge density or ionic strength.

METHOD

The particle surface is modeled as a smooth nonconducting plane surface to which is attached a layer of polyelectrolyte of thickness β consisting of

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N segments/unit area of effective hydrodynamic radius a distributed normal to the surface (in the x-coordinate direction) according to a normalized density distribution $\rho_s(x)$. Within this layer σ fixed charges/unit area are distributed normal to the surface according to a normalized density distribution $\rho_c(x)$. The suspending electrolyte solution, of viscosity η, dielectric constant ϵ, and characterized by a Debye-Huckel parameter κ, is able to freely penetrate this layer. The coordinate origin ($x = 0$) is placed at the outer edge of the polyelectrolyte layer, hence $\rho_c = \rho_s = 0$ for $x > 0$. The hydrodynamic shear plane is situated at $x = -r\beta$ where $0 \leq r \leq 1$. A more detailed discussion of the assumptions made in this model is given in Levine et al. (1983) but for brevity is not repeated here. However, note that all quantities are functions of x only. In particular, the effects of discrete charge are assumed to be negligible, especially at the lower ionic strengths that are of particular interest here.

The potential Ψ is related to the charge density $\sigma\rho_c$ by the Poisson-Boltzmann equation, expressed in dimensionless form as

$$\frac{d^2y}{dz^2} = \sinh y - 4\pi\rho_c\sigma/\epsilon, \tag{1}$$

where $y = \Psi e/kT$, $z = \kappa x$, e is the electronic charge, k is Boltzmann's constant, T is absolute temperature, $\kappa = (8\pi N_a e^2 I/1{,}000\,\epsilon kT)^{1/2}$, I is ionic strength, and N_a is Avogadro's number. The boundary conditions are

$$y \longrightarrow 0 \text{ as } z \longrightarrow \infty \tag{2}$$

$$\frac{dy}{dz} = 0 \text{ at } z = -\beta\kappa. \tag{3}$$

Eq. 3 implies that there are no charges on the surface of the membrane, i.e., that the outer monolayer of the bilayer consists of neutral and zwitterionic phospholipids.

Applying the boundary condition, Eq. 2, for $z > 0$, Eq. 1 has the solution

$$y = -2 \ln [\tanh (z - C)/2]. \tag{4}$$

In an analytical treatment the integration constant, C, would be determined by matching boundary conditions at $z = 0$. In the numerical approach, a guess was made, knowing that $0 < C < 20$ for the charge densities normally encountered. This guess was then refined numerically by using the second boundary condition, Eq. 3. To do this the region $-\beta\kappa \leq z \leq 0$ was divided up into m steps of length h. At $z = 0$, y, dy/dz, d^2y/dz^2 were known from the analytical solution, Eq. 4. The third to sixth differentials of y were obtained by repeated differentiation of Eq. 1, followed by substitution for y, dy/dz, d^2y/dz^2. The differentials were used to construct a sixth-order Taylor expansion around $z = 0$. Then y was evaluated at $z = -ih$, $i = 1$ to 4. Next dy/dz and d^2y/dz^2 for $i = 1$ to 3 were obtained from y by finite difference formulae. Having obtained the values of y and its first two derivatives at four consecutive points, Eq. 1 was integrated to $z = \kappa\beta$ numerically by the Adams Milne Bashforth predictor corrector method (for example see Burden et al., 1978). Since Eq. 1 was second order, the corrector equation had to be applied twice at each step, once to obtain dy/dz, and again to obtain y.

The value of C was then refined by bisection, where the next approximation was given by $C_{i+1} = (C_i + C_{i-1})/2$ or $C_{i+1} = (C_i + C_i - 2)/2$ depending on whether dy/dz at $z = -\beta\kappa$ was positive or negative. Eq. 1 was again integrated numerically using starting values calculated with the new guess for C. This procedure was repeated until Eq. 3 was satisfied to within 0.05 mV. Although this method of refining C has only first-order convergence, it is very safe, and since the functional dependence of dy/dz at $z = -\beta\kappa$ on C was not known, more powerful algorithms could not be applied easily.

The Navier-Stokes equation for this model, for a unit electric field is

$$\eta\frac{d^2u}{dz^2} - 6\pi a N\rho_s\eta u = \left(\frac{d^2\Psi}{dz^2} + 4\pi\rho_c\sigma/\epsilon\right)\epsilon/4\pi, \tag{5}$$

where u is the fluid velocity. The factor multiplying u in the second term is the friction component due to the fluid flow past the polyelectrolyte segments. The origin of this term is discussed more fully in Levine et al. (1983). The body force in the third term, arising from the interaction of the applied field with the net charge density of each fluid element, was derived from the values of d^2y/dz^2 obtained from the final numerical solution to Eq. 1. The boundary conditions for Eq. 1 were

$$u \longrightarrow U \text{ as } z \longrightarrow \infty \tag{6}$$

$$u = 0 \text{ at } z = -r\beta\kappa \tag{7}$$

where the velocity at infinity, U is equal and opposite in sign to the required electrophoretic mobility. Applying the boundary condition, Eq. 6, for $z > 0$, Eq. 5 has the solution

$$u = \epsilon\Psi/4\pi\eta + U. \tag{8}$$

In the analytical solution, the integration constant, U, would be determined by matching boundary conditions at $z = 0$. In the numerical approach, a guess was made, knowing that $0 < U < 5$. This guess was then refined by the same method as for the potential constant, C, using numerical integration of Eq. 5, until the boundary condition Eq. 7 was satisfied to the required accuracy.

Although the analytical solutions (Eqs. 4 and 8) were valid up to $z = 0$, better convergence for U was found if the numerical integration was started some distance outside the polyelectrolyte layer ($z = 0.2$ was arbitrarily chosen), since both ρ_c and ρ_s and their derivatives are identically zero in this region. This increased the accuracy of the Taylor expansion and reduced the amount of computation. The value of U obtained by this approach quickly converged to a stable value for $m > 100$.

The program was written in FORTRAN and run on an Amdahl 470 V8 computer (Amdahl Corp., Sunnyvale, CA) operating on the Michigan Terminal System. Evaluation of the mobility for one set of parameters, at one ionic strength using a 300 step integration took ~0.5 s of cpu time.

RESULTS AND DISCUSSION

To check on the accuracy of the program, four limiting charge and segment distributions, where analytical solutions were available, were calculated (Fig. 1). Curve A represents the case of a smooth particle, using the nonlinear Poisson-Boltzmann equation in the Smoluchowski relation (Eq. 26, Levine et al., 1983). There is a very good agreement between the analytical and numerical solutions at all concentrations.

The other three curves (from Eqs. 21–23, Levine et al., 1983) use the linear Poisson-Boltzmann equation, a uniform polyelectrolyte distribution of 70 Å thickness, with the charge placed at the particle surface (*B*), uniformly throughout the polyelectrolyte layer (*C*), and at the outer edge of the polyelectrolyte layer (*D*). Again the agreement is good at high ionic strengths, but as the ionic strength is decreased the mobility increases less rapidly for the numerical solutions, especially for the cases where the charge is concentrated in a plane (curves B, D), where at 10 mM the mobility is almost 1 μm s^{-1}/(V cm^{-1}) lower, a 50% decrease for case B. This divergence indicates that for the purpose of calculating the mobility, the linear equation significantly overestimates the potential for salt concentrations below 30 mM.

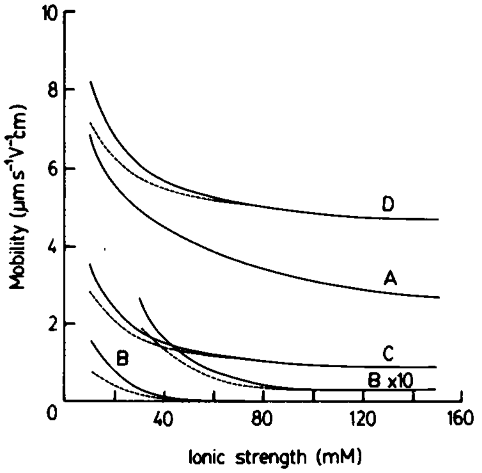

FIGURE 1 A comparison of mobilities calculated using the linear (——) and nonlinear (---) Poisson-Boltzmann equation is illustrated. Equations for the linear case were taken from Levine et al. (1983). Eqs. 26, 21, 22, and 23 were used for curves A, B, C, and D, respectively, with $\sigma = 1 \times 10^4$ esu/cm^2, $\beta = 70$ Å, $a = 6$ Å, $N = 5 \times 10^{13}$ segments/cm^2. The models represented are described in the text.

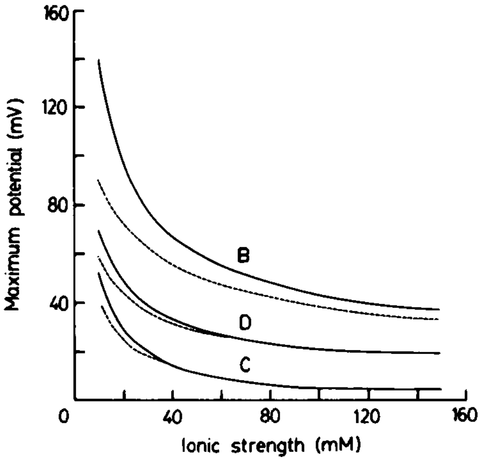

FIGURE 2 A comparison of maximum potentials in the polyelectrolyte layer calculated using the linear (——) and nonlinear (---) Poisson-Boltzmann equation is illustrated. Models and parmeters are the same as for Fig. 1.

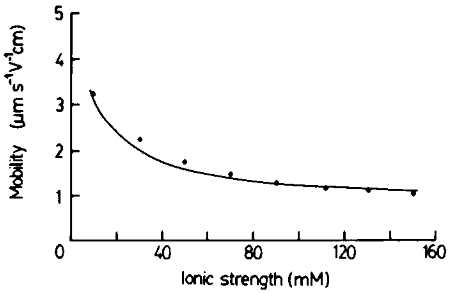

FIGURE 3 Electrophoretic mobility of human erythrocytes as a function of ionic strength is illustrated. ♦ indicates experimental data. Calculated values (——) for a uniform charge distribution, using the nonlinear Poisson-Boltzmann equation, with $\sigma = 1.065 \times 10^4$ esu/cm^2, $\beta = 78$ Å, $a = 7$ Å, $N = 3.24 \times 10^{13}$ segments/cm^2 are given.

To determine how large the potential must become before the nonlinear Poisson-Boltzmann equation must be used, the maximum potential within the polymer layer, y_m, which is located at $x = -\beta$, $-\beta \le x < 0$ for models B and C, and $x = 0$ for model D, was plotted as a function of ionic strength for both the linear and nonlinear cases (Fig. 2). From these curves it can be seen that the maximum potential for case C is lowest since the charge is spread out uniformly and only exceeds kT/e below 20 mM. Thus the linear model gives the mobilities for this case fairly accurately over the whole ionic strength range. Case D has lower potentials than case B since some of the counterions are in the polymer layer behind the charge plane, effectively doubling the screening effect of the electrolyte. For case B the nonlinear treatment gives significantly lower mobilities, even up to 50–60 mM, although the absolute difference is small since the mobilities are much lower than for the other two cases.

Using the uniform segment and charge density distributions from Levine et al. (1983), the thickness, β, and segment radius, a, were varied so as to obtain the best fit to the experimental data for fresh human erythrocytes (Heard and Seamen, 1960), Fig. 3. With $\beta = 78$ Å and $a = 7$ Å, a good fit was obtained at all ionic strengths down to 10 mM, without postulating an expansion of the polyelectrolyte layer as was done previously (Levine et al., 1983). In fact this result does not support the conclusion of Donath and Lerche (1980) that the layer thickness increases from 50 Å at 150 mM salt to 121 Å at 10 mM salt. The latter result was based on the linear treatment of Donath and Pastushenko (1980). The data in Fig. 2 do not rule out the expansion of the polyelectrolyte at lower ionic strengths (between 1 and 10 mM) reported by other groups (Geyer et al., 1977; Wolf and Gingell, 1983). However, since irreversible membrane changes may occur in this region (Heard and Seaman, 1960) interpreting electrophoretic mobility data by the models discussed here, which assume constant structural features, may be questionable.

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