Effect of Adsorbed Macromolecules on the Diffusiophoresis (in Electrolyte Gradients) of Charged Colloids

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ABSTRACT: The effect of adsorbed polyelectrolytes and uncharged polymers on the "diffusiophoresis" of charged colloids suspended in electrolyte gradients is investigated theoretically. It is known that the diffusiophoretic velocity of colloidal particles has two components: chemiphoretic and electrophoretic. Semianalytic expressions are derived for two parameters $\lambda^{(c)}$ and $\lambda^{(e)}$, which denote the *weighting factors* by which each of these velocity components is altered due to polymer adsorption. These factors are shown to depend on four dimensionless parameters: α, θ, B, and $\bar{\zeta}$ (or Σ), where α characterizes the distance to which the segments of the adsorbed polymer extend into the solution (and is the same as the "shielding ratio" defined by Varoqui and Dejardin),[4] θ characterizes a dimensionless Debye length, B corresponds to the degree of dissociation of the ionizable groups of the adsorbed polyelectrolyte, and $\bar{\zeta}$ (or Σ) is the zeta potential (or surface charge density) of the particle. The alteration in the particle's velocity due to polymer adsorption is estimated for various values of these dimensionless parameters. It is observed that polyelectrolyte adsorption, in certain situations, could lead to (i) particle migration velocities higher than those possible with "clean" particles under otherwise identical conditions and (ii) a reversal in the direction of migration. The adsorption of uncharged polymers, on the other hand, leads to a reduction in the particle velocity, if the two parameters $\bar{\zeta}$ and β—a normalized dimensionless mobility difference of the two ions of the electrolyte—have the same sign. However, when $\bar{\zeta}$ and β are of opposite signs, a reversal in the direction of particle migration is possible even with uncharged polymers under some conditions. Finally, an offshoot of the present analysis is the additional result that $\lambda^{(e)}$ also represents the factor by which adsorbed polyelectrolytes/uncharged polymers alter the *electrophoretic mobilities* of colloidal particles subjected to electrophoresis by an externally applied electric field.

1. Introduction

It is well-known that the adsorption of long-chain molecules such as polymers and proteins, and even certain surfactants, on charged colloidal particles can significantly affect the electrokinetic migration velocities of these particles. The observed changes in the migration velocities can result from the charge as well as the structural (i.e., conformational) characteristics of these adsorbed macromolecules: the conformational characteristics of the adsorbed layer affect the additional hydrodynamic drag force offered by this layer when the particle migrates, while the charge on the segments of the adsorbed chains, if any, affects the electrical potential field around the particle and as a result the net driving force for its migration.

It has been recently suggested that a study of the electrokinetic behavior of a solid substrate with an adsorbed polymer layer can provide a means of characterizing, in an average sense, the conformational structure (i.e., the segmental density distribution normal to the substrate's surface) of the adsorbed layer.[1] Indeed, Cohen Stuart et al.[1-3] defined a so-called "electrokinetic thickness" for the adsorbed layer, which could be deduced by comparing the electrophoretic velocity in the presence and absence of adsorbed macromolecules. It was also indicated that[1] when dealing with charged adsorbents, the measurement of electrokinetic thickness can form a more sensitive probe for characterizing the adsorbed polymer structure in comparison to the measurement of the so-called "hydrodynamic thickness",[4,5] because the former depends on the ionic strength of the medium while the latter does not.

Evidently, the three-dimensional structure of an adsorbed macromolecular layer plays an important role in the electrokinetic behavior of biocolloids as well. It has been recognized recently that one has to take into account the precise spatial distribution of the segments of the adsorbed glycoproteins and glycolipids (glycocalix) present on the surface of human red blood cells, and the resulting extra hydrodynamic drag force, in order to account properly for the observed electrophoretic velocities of these erythrocytes.[6-8] The migration exhibited by certain mammalian cells under the influence of the concentration gradient of a chemical stimulant (a phenomenon known as chemotaxis[9,10]) may very likely be affected when macromolecules are adsorbed on the surfaces of these cells. While the chemosensory mechanism responsible for such a migration could be quite different for different classes of cells,[10] it appears that, at least, in some cases this phenomenon is closely related to the well-established phenomenon of "diffusiophoresis" of colloidal particles.[11,12]

Diffusiophoresis is the migration of colloidal particles in a solution having inhomogeneities in its solute concentration.[13-19] If the solute is nonelectrolytic, the particle moves toward or away from a region of higher solute concentration, depending on whether the solute is attracted to or repelled from the particle surface.[14,16] Diffusiophoresis in electrolytic media is, however, more involved and is explained as an electrokinetic migration of the charged particle resulting from two effects: (i) the polarization of the diffuse double layer surrounding the particle (*chemiphoretic* component) and (ii) the macroscopic electric field—diffusion potential–that arises in the electrolyte solution due to differences in the mobilities of the two ions of the electrolyte (*electrophoretic* component). The expressions necessary for

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quantitatively predicting the diffusiophoretic velocities of the colloidal particle as a function of the radius of the particle and the solute concentration were derived recently by Anderson, Prieve, and their collaborators.[15-18]

The objective of this work is to predict the effect of adsorbed macromolecules, both uncharged and charged, on the diffusiophoretic velocity of a charged colloidal particle suspended in an electrolyte solution of *known* concentration gradient. Such information may prove relevant in understanding (i) conformational characteristics of adsorbed polymers, (ii) chemotactic transport of cells in physiological media, and (iii) colloidal separations that are based on physicochemical traits of the particles.

2. Development of the Model

This section begins with a very brief outline of the classical Gouy–Chapman description of the equilibrium double layer around a charged colloidal particle, which is then used to delineate the phenomenon of diffusiophoresis and to derive an expression for the diffusiophoretic velocity of the particle. The details of this derivation follow very closely the approach used by Prieve et al.[17] Next, the extension of the theory to a particle with an adsorbed neutral or charged polymer is described.

2.1. Equilibrium Double Layer around a Colloidal Particle. Let us imagine that a rigid colloidal particle having fixed charges on its surface is immersed in a polar solvent containing a completely dissociated symmetric binary electrolyte at a *uniform* bulk concentration, C_∞. Counterions in the solution, i.e., ions with charge opposite in sign to that of the fixed charges of the particle, get attracted toward the paricle while the co-ions in the solution, i.e., ions whose charges have the same sign as the fixed charges of the particle, are repelled from it. Brownian motion, on the other hand, tends to oppose the motion of the ions caused by this electrostatic attraction (or repulsion). If the solution is dilute, the net flux of the ions, $\mathbf{N}_\pm$, toward (or away from) the particle is given by the Nernst–Planck equation

$$\mathbf{N}_\pm = -D_\pm\left[\nabla C_\pm \pm \frac{ZeC_\pm}{kT}\nabla\Psi\right] \qquad (1)$$

where + and − signs denote, respectively, the cations and the anions, D and C represent the diffusion coefficient and the local number concentration of these ions, Z is the absolute value of the valency of the ions, Ψ is the local electrostatic potential, e is the protonic charge, k is the Boltzmann constant, and T is the absolute temperature. When equilibrium is reached, the net flux of the ions becomes zero, thereby giving rise to the following Boltzmann distribution for the concentration of the ions in the direction normal to the particle's surface

$$C_\pm = C_\infty \exp(\mp(\phi)) \qquad (2)$$

where ϕ is given by

$$\phi = \frac{Ze(\Psi - \Psi_\infty)}{kT}$$

The particle's surface (with its fixed charges) and the region of the solution with a *diffused distribution* of charges surrounding this surface are together called an electrical double layer. The electrostatic potential distribution in the diffuse charge layer is governed by Poisson's equation:

$$\nabla^2\Psi = -\frac{4\pi}{\epsilon}\rho^* = -\frac{4\pi}{\epsilon}Ze(C_+ - C_-) \qquad (3)$$

Here ρ^* represents the local volumetric charge density and ϵ the dielectric constant of the medium. Combining eq 2 with Poisson's equation gives rise to the Poisson–Boltzmann equation

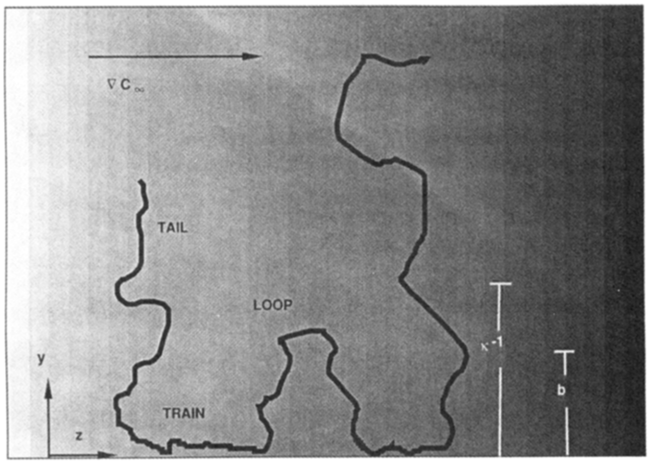

Figure 1. Schematic of the microenvironment of a colloidal particle suspended in an electrolyte gradient when it has an adsorbed polymer on it. The intensity of darkness at any location in the drawing is a measure of the local electrolyte concentration. y and z represent the coordinate axes.

$$\nabla^2\phi = \kappa^2 \sinh \phi \qquad (4)$$

where $\kappa^2 = (8\pi Z^2e^2C_\infty)/(\epsilon kT)$. $1/\kappa$ signifies the characteristic distance over which the potential drops to its asymptotic value in the fluid far away from the particle and is called either the "Debye length" or the "double-layer thickness". When describing the phenomena within the double layer, the curvature of the particle's surface may be ignored provided the double layer is differentially thin; i.e., the thickness of the double layer, $1/\kappa$, is almost insignificant compared to the smallest principal radius of curvature, R, at any point on the particle's surface. Under these conditions, the particle surface and the region of the solution surrounding it, but lying within the double layer, could be described by employing a *locally planar* coordinate system (x, y, z), where the coordinate y represents the direction perpendicular to the particle's surface and the coordinates x and z represent the directions parallel to the surface of the particle at the chosen location (see Figure 1). In this representation, eq 2 takes the form

$$C_\pm(y) = C_\infty \exp(\mp\phi(y)) \qquad \phi(y) = Ze\left(\frac{\Psi(y) - \Psi_\infty}{kT}\right) \qquad (5)$$

Equation 4 can now be integrated from the surface of the particle (where $\Psi = \Psi_S$) to a distance far removed from the particle surface (where $\Psi = \Psi_\infty$) to obtain the following equation for the potential distribution in the fluid around the particle

$$\tanh\left(\frac{\phi(y)}{4}\right) = \gamma e^{-\kappa y} \qquad (6)$$

where $\gamma = \tanh(Ze\zeta/4kT)$ with $\zeta = (\Psi_S - \Psi_\infty)$.

2.2. Diffusiophoresis of a Bare Colloidal Particle. Assume now that the *bulk* electrolyte solution, instead of being at a uniform concentration (C_∞), has a concentration *gradient*. This concentration gradient drives the diffusion of the dissociated ions of the electrolyte in the direction of the gradient. If the mobilities of the two ions of the electrolyte are unequal, an electrostatic potential field, $\mathbf{E}_\infty$, develops spontaneously in the direction of the concentration gradient in order to equalize the fluxes of both types of ions and thus to preserve the electroneutrality within the system. From eq 1, we can write the following expressions for the potential field, $\mathbf{E}_\infty$, and for the net flux of the electrolyte, $\mathbf{N}_\infty$

$$\mathbf{E}_\infty \equiv -\nabla \Psi_\infty = \frac{kT}{Ze} \beta \nabla \ln C_\infty \qquad (7)$$

where

$$\beta = \frac{D_+ - D_-}{D_+ + D_-}$$

and

$$\mathbf{N}_\infty = -D \nabla C_\infty \qquad (8)$$

where

$$D = \frac{2D_+ D_-}{D_+ + D_-}$$

The subscript ∞ in eqs 7 and 8 indicates the undisturbed *bulk* solution.

Now, when a charged colloidal particle is placed in the above solution, the particle migrates parallel to the concentration gradient of the electrolyte. This motion of the colloidal particle under the influence of a concentration gradient of a solute, as noted in the Introduction, is called diffusiophoresis. The precise direction—i.e., whether the particle moves "uphill" or "downhill" of the solute gradient—and the speed of the particle depend on the surface charge density of the particle, the valence number and the diffusivities of the ions of the electrolyte, and the magnitude of the concentration gradient of the electrolyte. As already noted, Prieve et al. described this entire phenomena in a lucid manner and presented some elegant analytical[15,17] and numerical[18] solutions for the motion of the particle, which take into consideration the effect of the particle's curvature on its migration velocity. Their analysis reveals, however, that when $\kappa^{-1} \ll R$ (the smallest principal radius of curvature at any point on the particle's surface), the velocity of the particle simply equals the velocity acquired by an *infinite flat plate* when an electrolyte gradient of the same magnitude is imposed parallel to its surface. Prieve et al. have also demonstrated experimentally this phenomenon of diffusiophoresis recently and confirmed that the experimentally measured particle migration velocities are in excellent agreement with their theoretical predictions.[19] We will describe below briefly those features of these authors' theory that have relevance to the present work. We will restrict our discussion to the case of $\kappa^{-1} \ll R$ (i.e., to the case of an infinite flat plate with electrolyte gradient in the z direction; see Figure 1).

Though the electrolyte solution bathing the plate is not strictly in equilibrium (due to nonzero N_z), the concentration of the ions in the y direction can still be approximated by the Boltzmann distribution (i.e., eq 5) provided $|\mathrm{d} \ln C_\infty/\mathrm{d}z| \ll \kappa$. Equation 5, now, is of the form

$$C_\pm(z,y) = C_\infty(z) \exp(\mp\phi(z,y)) \qquad (9)$$

where

$$\phi(z,y) = \frac{Ze(\Psi(z,y) - \Psi_\infty(z))}{kT}$$

Furthermore, if the z component of the potential field is significantly smaller than the y component, eq 6 can still be used to represent the potential distribution in the y direction, i.e.

$$\tanh\left(\frac{\phi(z,y)}{4}\right) = \gamma(z) e^{-\kappa y} \qquad (10)$$

where now

$$\gamma(z) = \tanh\left[\frac{Ze\zeta(z)}{4kT}\right] \qquad \kappa^2 = \frac{8\pi Z^2 e^2 C_\infty(z)}{\epsilon kT}$$

$$\zeta(z) = \Psi_s(z) - \Psi_\infty(z)$$

Accounting for the electrostatic potential field, the equation of momentum for the charged fluid elements within the diffuse layer extending from the plate will be

$$-\eta \nabla^2 \mathbf{V} + \nabla p + (C_+ - C_-) Ze \nabla \Psi = \mathbf{0} \qquad (11)$$

Since it can be proved from the equation of continuity that V_z is the only significant velocity component, substituting eq 9 into eq 11 and then integrating the y component of the resultant equation yields the following expression for the variation of fluid pressure in the y direction:

$$p(z,y) - p_\infty = 2kTC_\infty(z)\{\cosh[\phi(z,y)] - 1\} \qquad (12)$$

Inserting this expression for the pressure profile along with eqs 9 and 10 into the z component of eq 11 and then integrating twice results in the following analytical relation for the velocity of the plate (U_0) relative to the bulk fluid:

$$U_0 = -[V_z(y\rightarrow\infty) - V_z(y=0)] = -\frac{\epsilon\zeta}{4\pi\eta}\frac{\mathrm{d}\Psi_\infty}{\mathrm{d}z} - \frac{4kT}{\kappa^2\eta} \ln(1-\gamma^2) \frac{\mathrm{d}C_\infty}{\mathrm{d}z} \qquad (13)$$

The first and second terms on the right-hand side of eq 13 denote, respectively, the electrophoretic ($U_0^{(\mathrm{e})}$) and chemiphoretic ($U_0^{(\mathrm{c})}$) contributions to the total mobility (U_0) of the particle. The axial electric potential gradient ($\mathrm{d}\Psi_\infty/\mathrm{d}z$) to which $U_0^{(\mathrm{e})}$ owes its existence is, as mentioned earlier, the macroscopic *diffusional potential* gradient (given by eq 7) that arises from the unequal mobilities of the two ions of the electrolyte. However, it should be noted that the above expression for $U_0^{(\mathrm{e})}$ remains valid even if there is an externally applied potential gradient on the system in addition to (or instead of) the diffusion potential. In this latter situation, $\mathrm{d}\Psi_\infty/\mathrm{d}z$ simply equals the algebraic sum of the two electric fields. The chemiphoretic contribution, $U_0^{(\mathrm{c})}$, on the other hand, exists always as long as there is a concentration gradient for the dissolved electrolyte in the solution and is always oriented in the direction of higher salt concentration. We can, therefore, write, using the definition of κ, that

$$\mathbf{U}_0 = \mathbf{U}_0^{(\mathrm{e})} + \mathbf{U}_0^{(\mathrm{c})} \qquad (14)$$

where

$$\mathbf{U}_0^{(\mathrm{c})} = -\frac{\epsilon}{2\pi\eta}\left[\frac{kT}{Ze}\right]^2 \ln(1-\gamma^2) \nabla \ln C_\infty \qquad (15)$$

and

$$\mathbf{U}_0^{(\mathrm{e})} = \frac{\epsilon\bar{\zeta}}{4\pi\eta}\left(\frac{kT}{Ze}\right)(-\nabla\Psi_\infty) \qquad (16a)$$

when there is an externally applied electric field or

$$\mathbf{U}_0^{(\mathrm{e})} = \frac{\epsilon\beta\bar{\zeta}}{4\pi\eta}\left(\frac{kT}{Ze}\right)^2 \nabla \ln C_\infty \qquad (16b)$$

when there is only diffusional potential, with $\bar{\zeta} = (Ze\zeta/kT)$.

For small and large values of $|\bar{\zeta}|$, the $\ln(1-\gamma^2)$ term in eq 15 can be approximated by the asymptotic expressions

$$\ln(1-\gamma^2) \cong \begin{cases} -\left[\dfrac{\bar{\zeta}}{4}\right]^2 & \text{for } \dfrac{|\bar{\zeta}|}{4} \ll 1 \\ -\dfrac{|\bar{\zeta}|}{2} & \text{for } \dfrac{|\bar{\zeta}|}{4} \gg 1 \end{cases} \tag{17}$$

which, when substituted into eq 15, lead to the following limiting equations for $\mathbf{U}_0$ in the absence of an externally applied electric field:

$$\mathbf{U}_0 \cong \begin{cases} [\beta\bar{\zeta} + (\bar{\zeta}^2/8)]\dfrac{\epsilon}{4\pi\eta}\left[\dfrac{kT}{Ze}\right]^2 \nabla \ln C_\infty & \text{for } \dfrac{|\bar{\zeta}|}{4} \ll 1 \\ [\beta\bar{\zeta} + |\bar{\zeta}|]\dfrac{\epsilon}{4\pi\eta}\left[\dfrac{kT}{Ze}\right]^2 \nabla \ln C_\infty & \text{for } \dfrac{|\bar{\zeta}|}{4} \gg 1 \end{cases} \tag{18}$$

It is clear from eq 18 that, for small values of $(|\bar{\zeta}|/4)$, $\mathbf{U}_0^{(c)} \ll U_0^{(e)}$ since $(\bar{\zeta}^2/8)$ is much smaller than $|\beta\bar{\zeta}|$; i.e., the velocity of the particle essentially equals its electrophoretic component. However, as $|\bar{\zeta}|$ is raised, the contribution of $U_0^{(c)}$ to U_0 becomes more appreciable and $|U_0^{(c)}| \sim |U_0^{(e)}|$ for sufficiently large value of $|\bar{\zeta}|$. Indeed, for very large values of $(|\bar{\zeta}|/4)$, $|U_0^{(c)}|$ becomes greater than $|U_0^{(e)}|$ provided $|\beta| < 1$, as can be seen from eq 18; i.e., the particle, now, migrates in the direction of increasing salt concentration regardless of the sign of $\bar{\zeta}$. As will be shown later, this insight regarding the dependence of the diffusiophoretic velocity of the bare colloidal particle on the magnitude of $\bar{\zeta}$ proves useful in understanding the role of adsorbed polymers.

We note in passing that, in order to compute the diffusiophoretic velocity of a particle with a fixed surface charge density (σ), the dimensionless surface potential, $\bar{\zeta}$, appearing in the above expressions can be determined by using the following expression[36]

$$\sigma = \left(\frac{\epsilon}{2\pi}\frac{kT}{Ze}\kappa\right)\sinh\left(\frac{\bar{\zeta}}{2}\right) \tag{19}$$

2.3. Diffusiophoresis of a Colloidal Particle with Adsorbed Polymer.

Now suppose that the colloidal particle has, in addition to the fixed charges, some adsorbed polymer (either charged or uncharged) on its surface. The objective of the present work is, as noted in the Introduction, to investigate the effect of this adsorbed polymer layer on the diffusiophoretic velocity of the particle.

Besides assuming that the double layer is differentially thin, let us further assume that the characteristic distance to which the segments of the adsorbed polymer extend into the solution is also significantly smaller than the smallest principal radius of curvature (R) at any point on the particle's surface. These two assumptions together permit us to use, once again, the *infinite flat plate approach* for predicting the migration velocity of the particle. The fluid elements within the double layer now experience an extra drag force from the adsorbed polymer layer. In view of this, the equation of momentum for the fluid within the double layer will be

$$\eta\nabla^2\mathbf{V} - f\rho_p(y)\mathbf{V} - \nabla p - (C_+ - C_-)Ze\nabla\Psi = \mathbf{0} \tag{20}$$

where $\rho_p(y)$ is the local number density of the polymer segments, η is the local viscosity of the *suspension*, and f is the local friction coefficient *per* polymer segment.

The omission of the inertial force terms in the equation of momentum is justified on the ground that the Reynolds number based on the diffusiophoretic velocity of the particle and its size will be within the creeping flow limits. The first, third, and fourth terms in the above equation account, respectively, for the viscous, pressure, and electrostatic forces acting on the fluid while the second term represents the drag force due to the adsorbed polymer layer. The quantities η and f appearing in the first and second terms are, actually, functions of the *local* number density of polymer segments, $\rho_p(y)$, due to hydrodynamic interactions among segments.[5,33] However, it was shown by Anderson and Kim that use of the *solvent* viscosity for η and the friction coefficient of an *isolated* polymer segment for f (i.e., neglecting hydrodynamic interactions among segments) constitutes very good approximations in accounting for the drag of adsorbed polymers on flow past solid surfaces.[33] Hence, in what follows, we shall incorporate these assumptions. It should also be noted that while *Stoke's law* for flow past a sphere provides a reasonable estimate of f when the polymer segment is uncharged, estimation of the value of f for charged segments should be based on a theory that takes into account the fact that the fluid flowing past the stokeslet carries a volumetric charge density.[13]

Clearly, a knowledge of $\rho_p(y)$ is needed prior to solving eq 20 for the velocity of the particle. We shall, therefore, review below very succinctly some of the theoretical approaches available in the literature for estimating the segment density distribution (SDD) of the adsorbed layer. It should be noted that SDD is a function of (i) the physicochemical properties of the polymer and of the adsorbing surface and (ii) the nature of the solvent.

Review of Theories for Predicting the Segment Density Distribution of Adsorbed Polymers. Figure 1 shows the typical conformation of an adsorbed linear flexible homopolymer. In general, there are at least three different segment sequences, namely, trains, loops, and tails. Trains represent those portions of the adsorbed molecule where all the segments lie within the adsorbing plane while loops represent those segment sequences where all the segments are in contact with the solution but for the two segments on either end which are in contact with the adsorbing plane. Tails are similar to loops except that only one end of the segment sequence lies within the adsorbing plane while the other end dangles freely within the solution.

Though a number of theories are available in the literature for the adsorption of flexible homopolymers, only a few of these have addressed the subject of adsorption of multiple chains while properly accounting for the segment–segment, segment–solution, and segment–adsorbing surface interactions. Of relevance to us amongst these are the theories due to Hoeve, Silberberg, Roe, Schuetjens and Fleer, Edwards, de Gennes, Dolan and Edwards, Helfand, Richmond and Jones, and Ploehn et al.[20-29] However, the theories of Hoeve and Silberberg[20,21] assume, a priori, exponential and step function forms, respectively, for the segment density distribution of the adsorbed layer. On the other hand, the self-consistent-field (SCF) lattice theories of Roe and of Scheutjens and Fleer[22,23] and the self-consistent-field continuum theories of Edwards, de Gennes, Dolan and Edwards, Helfand, Richmond and Jones, and Ploehn et al.[24-29] do not require any a priori assumptions regarding the functional form of the segment density distribution. In these theories, the SDD arises automatically by solving the SCF equation in which the potential field acting on each segment depends upon the local density distribution itself. Of these SCF theories, the theory of Scheutjens and Fleer[23] provides an accurate description of the overall segment density distribution as well as the density distribution of each kind of segment sequence, i.e., trains, loops, and tails.

When the adsorbed polymer is *charged* (i.e., a polyelectrolyte), there are not many theoretical treatments available in the literature to describe its segment density distribution. One of the first theoretical treatments for polyelectrolyte adsorption is by Hesselink,[30] who extended Hoeve's theory for the adsorption of uncharged homopolymers. In contrast to the exponential density distribution assumed by Hoeve, Hesselink assumed in his theory a step function for the segment density distribution of the adsorbed layer. Papenhuijzen et al.[32] have recently extended the SCF lattice model of Roe[22] for uncharged homopolymers to the case of polyelectrolytes. Since Roe's model ignores end effects (i.e, the presence of tails), this new model for polyelectrolytes also accounts only for the presence of loops and trains. However, Van der Schee and Lyklema[31] report a few preliminary results obtained by extending Scheutjens and Fleer's model, which also accounts for the presence of tails.

Semianalytical Expression for the Velocity of the Particle. While some of the theories described above provide a very accurate description for the segment density distribution of the adsorbed layer, incorporating them in a rigorous manner into eq 20 makes it computationally very difficult and time consuming. Fortunately, Ploehn et al.'s[29] analytical solution of the SCF equation for uncharged polymers, valid for so-called "ground-state dominated" systems, reveals an exponential functional form for the segment density distribution in a Θ solvent. For this reason, we decided to represent $\rho_P(y)$ in terms of a single-exponential distribution, which makes the equation of momentum much more amenable from the mathematical point of view without sacrificing too much on the accuracy. In their study on fluid dynamical effects of adsorbed polymers on particles, Anderson and Kim[33] assumed a double-exponential distribution, one accounting for the fast decaying loops and the other accounting for the slow decaying tails, in order to obtain a better approximation for the overall segment density distribution. It has been shown by these authors and other investigators in the past[5] that tails are the chief contributors to the total drag force offered by the adsorbed polymer layer. In light of this, the single-exponential form that we use in the present study can be imagined to be accounting mainly for the distribution of tails. Replacing $\rho_P(y)$ with this single-exponential form transforms eq 20 into

$$\eta\nabla^2\mathbf{V} - f\rho_P{}^0 \exp\left(-\frac{y}{b}\right)\mathbf{V} - \nabla p - (C_+ - C_-)Ze\nabla\Psi = 0 \qquad (21)$$

where $\rho_P{}^0$ is the number density of the segments at the particle–fluid interface and b is a characteristic distance over which the segment density drops to its asymptotic value. It should be noted that, for polyelectrolyte adsorption, the assumed exponential decay of SDD is, perhaps, not quite valid at low ionic strengths and high degrees of charging of the polymer molecules. However, the recent SCF computations of Van der Schee and Lyklema (Figure 2 of ref 31) as well as the small-angle neutron-scattering experiments of Cosgrove, Obey, and Vincent (Figures 8 and 10 of ref 38) do indicate that, even when the degree of charging of the polyelectrolyte molecules is 100%, the shape of the SDD is not grossly different from the exponential form for ionic strength values greater than or equal to 0.5 M. In view of these observations, one could probably assume the exponential form to be a reasonable representation, at least qualitatively, even for ionic strengths smaller than 0.5 M, at *low* degrees of dissociation of the polyelectrolyte.

With the fact that V_z is the only significant component of the velocity, $\mathbf{V}$, of the fluid (which can be shown easily by an order of magnitude analysis of the equation of continuity), eq 21 can be decomposed into its component equations as follows:

$$z \text{ component} \qquad \eta\frac{\partial^2 V_z}{\partial y^2} - f\rho_P{}^0 \exp\left(-\frac{y}{b}\right)V_z - \frac{\partial p}{\partial z} - (C_+ - C_-)Ze\frac{\partial\Psi}{\partial z} = 0 \qquad (22)$$

$$y \text{ component} \qquad -\frac{\partial p}{\partial y} - (C_+ - C_-)Ze\frac{\partial\Psi}{\partial y} = 0 \qquad (23)$$

Since the y component equation remained unchanged even when an adsorbed polymer layer is present on the surface of the particle, the pressure profile obtained after integrating it will be the same as that given in eq 12. Incorporating this pressure profile into the z component of the equation of momentum leads to

$$\eta\frac{\mathrm{d}^2 V_z}{\mathrm{d}y^2} - f\rho_P{}^0 \exp\left(-\frac{y}{b}\right)V_z = 2kT\left\{[\cosh\phi(z,y) - 1]\frac{\mathrm{d}C_\infty}{\mathrm{d}z} - C_\infty \sinh\phi(z,y)\frac{Ze}{kT}\frac{\mathrm{d}\Psi_\infty}{\mathrm{d}z}\right\} \qquad (24)$$

Note that, in the absence of any externally applied electric field, $\mathrm{d}\Psi_\infty/\mathrm{d}z$ in the above equation will still be given by eq 7. Also, if the adsorbed polymer is uncharged, the potential field $\phi(z,y)$ in the above equation can still be described by eq 10, provided one assumes that the effect of polymer segments on the dielectric properties of the medium can be accounted for via an *effective* dielectric constant. However, if the adsorbed polymer is charged, the expression for $\phi(z,y)$ should be modified to account for the fact that the total local volumetric charge density, ρ^*, in the Poisson equation (eq 3) now has two contributions: (i) from the fixed charges on the segments of the adsorbed polymer chains and (ii) from the diffused cloud of mobile ions of the electrolyte in the solution. When the Boltzmann distribution (i.e., eq 9) is used to describe the concentration of the mobile charges, the modified Poisson–Boltzmann equation can be written as

$$\frac{\partial^2\phi(z,y)}{\partial y^2} = \kappa^2\left[\sinh\phi - A\exp\left(-\frac{y}{b}\right)\right] \qquad (25)$$

where κ^2 is as defined earlier and $A = (\rho_P{}^0 Z')/(2ZC_\infty)$, with Z' denoting the valence number corresponding to the average amount of fixed charge per segment of the polyelectrolyte. (Note that Z' need not be an integer.) Solving the above equation, subject to the boundary conditions

$$\phi(z,y) \equiv \frac{Ze}{kT}[\Psi(z,y) - \Psi_\infty(z)] \rightarrow 0 \qquad \text{as } y \rightarrow \infty \qquad (26)$$

and

$$\phi(z,y) \equiv \frac{Ze}{kT}[\Psi_s(z) - \Psi_\infty(z)] = \bar{\zeta} \qquad \text{at } y = 0 \qquad (27a)$$

or

$$\frac{\partial\phi}{\partial y} = -\frac{4\pi Ze}{\epsilon kT}\sigma \qquad \text{at } y = 0 \qquad (27b)$$

gives the electrostatic potential distribution in the y direction. Equation 27a is the appropriate boundary condition when the zeta potential (ζ) of the particle is known, while eq 27b provides a suitable boundary condition when the surface charge density (σ) of the particle is given. After substituting the potential distribution, $\phi(z,y)$, into eq 24, one can, in principle, solve the latter equation with the following boundary conditions to obtain the velocity distribution of the fluid surrounding the particle:

$$\text{at } y = 0, \quad V_z = 0 \tag{28}$$

$$\text{as } y \to \infty, \quad V_z \text{ remains finite} \tag{29}$$

However, in its present form, eq 24 does not admit a simple analytical solution. Nevertheless, with application of the following logarithmic transformation of the y coordinate (suggested by de Gennes in a personal communication to Varoqui and Dejardin[4]), this equation can be transformed into a form that can be solved to obtain a *semianalytic* expression for the diffusiophoretic velocity of the particle

$$t = 2\alpha e^{-y/2b} \tag{30a}$$

where

$$\alpha \equiv (b/l) = b/[\eta/f\rho_P{}^0]^{1/2} \tag{30b}$$

The parameter α, which is a ratio of two characteristic lengths, is the so-called "shielding ratio" defined by Varoqui and Dejardin,[4] and its magnitude provides a measure of the hydrodynamic resistance offered by the polymer during flow past the particle.

In terms of this new variable "t", the transformed z component of the equation of momentum and its boundary conditions (i.e., eqs 28 and 29) will be

$$t^2\frac{\mathrm{d}^2V_z}{\mathrm{d}t^2} + t\frac{\mathrm{d}V_z}{\mathrm{d}t} - t^2V_z = \left[\frac{8b^2kT}{\eta}\right]h(t) \tag{31a}$$

where

$$h(t) \equiv h_c(t) + h_e(t) = \left\{\frac{\mathrm{d}C_\infty}{\mathrm{d}z}[\cosh\phi(t) - 1]\right\} + \left\{C_\infty\left[-\frac{\mathrm{d}\Psi_\infty}{\mathrm{d}z}\right]\sinh\phi(t)\right\} \tag{31b}$$

and

$$\text{at } t = 2\alpha, \quad V_z = 0 \tag{32}$$

$$\text{as } t \to 0, \quad V_z \text{ remains finite} \tag{33}$$

As can be noted from eq 31b, for prespecified values of electrolyte and potential gradients in the bulk solution ($\mathrm{d}C_\infty/\mathrm{d}z$ and $\mathrm{d}\Psi_\infty/\mathrm{d}z$), the form of the forcing function $h(t)$ is determined by the functional dependence of ϕ upon t—or equivalently y—which, in turn, is obtained by solving eq 25. It also proves convenient for later discussion to identify separately, as shown in eq 31b, the contributions from chemiphoresis ($h_c(t)$) and electrophoresis ($h_e(t)$) to the function $h(t)$. The *homogeneous* part of eq 31a can be reduced into a standard Bessel's equation, and its solution can be expressed in terms of the modified zero-order Bessel functions of the first and second kind, i.e., $I_0(t)$ and $K_0(t)$. When one knows the *complementary function*, the *particular solution* for a given forcing function, $h(t)$, can be found by the method of *variation of parameters*.[34] When the total solution thus determined is used, the velocity of the plate relative to the fluid, U_P, can be written as

$$U_P \equiv -V_z(y\to\infty) = \left[\frac{8b^2kT}{\eta}\right]\left\{\int_0^{2\alpha}\frac{h(t)}{t}[K_0(t) - GI_0(t)]\,\mathrm{d}t\right\} \tag{34}$$

where

$$G = \frac{K_0(2\alpha)}{I_0(2\alpha)}$$

While eq 34 provides an explicit expression for the diffusiophoretic velocity, the evaluation of the definite integral contained in this expression can be carried out only after establishing the functional form for the forcing function, $h(t)$. The functional dependence of $h(t)$ upon t, as already noted, will vary depending on whether the adsorbed polymer is uncharged or charged. Before we proceed with the task of establishing $h(t)$, it proves useful to decompose eq 34 into its components and rearrange them in a suitable dimensionless form.

Decomposition of the Total Particle Velocity into Components and Dedimensionalization. Equation 34, which provides the diffusiophoretic velocity of an arbitrarily shaped particle when $\kappa R \gg 1$, can be written, just as in the case of a bare colloidal particle, as the sum of electrophoretic ($U_P{}^{(e)}$) and chemophoretic ($U_P{}^{(c)}$) contributions:

$$U_P = U_P{}^{(e)} + U_P{}^{(c)} \tag{35}$$

This decomposition of U_P into its components is possible because *the forcing function $h(t)$, as shown above, is made up of a simple sum of $h_e(t)$ and $h_c(t)$*. Separate evaluation of the component velocities, $U_P{}^{(e)}$ and $U_P{}^{(c)}$, can be carried out by simply replacing $h(t)$ in eq 34 by $h_e(t)$ and $h_c(t)$, respectively:

$$U_P{}^{(e)} = \left[\frac{(\alpha/\theta)^2\epsilon}{\pi\eta}\left(\frac{kT}{Ze}\right)(-\nabla\Psi_\infty)\right]\left\{\int_0^{2\alpha}\frac{\sinh\phi(t)}{t}[K_0(t) - GI_0(t)]\,\mathrm{d}t\right\} \tag{36}$$

$$U_P{}^{(c)} = \left[\frac{(\alpha/\theta)^2\epsilon}{\pi\eta}\left(\frac{kT}{Ze}\right)^2\nabla\ln C_\infty\right]\left\{\int_0^{2\alpha}\frac{[\cosh\phi(t) - 1]}{t}\times[K_0(t) - GI_0(t)]\,\mathrm{d}t\right\} \tag{37}$$

In writing eqs 36 and 37, the definition of κ is used to replace C_∞, and the dimensionless parameter θ, which is the ratio of the thickness of the diffuse layer (κ^{-1}) to the characteristic length l (defined in eq 30b), and the shielding ratio, α (defined in eq 30a), are introduced. Once again, $-\nabla\Psi_\infty$ in eq 36 can solely be due to differences in ion mobilities (in which case it is still given by eq 7) or can be due to an externally applied electric field. In the latter situation, eq 36 represents a modification of the Helmholtz equation (for the electrophoretic velocity of a colloidal particle) due to the presence of adsorbed polymer.

Next, we express each of the above velocity components as a *normalized* component, $\lambda^{(i)}$ (i = c, e), defined as the ratio of the velocity component in the presence of the adsorbed polymer layer to its value in the absence of the layer. Since eqs 15 and 16a provide the expressions for the electrophoretic and chemiphoretic components of the migration velocity of a bare colloidal particle, one can write

$$\lambda^{(e)} \equiv \frac{U_P{}^{(e)}}{U_0{}^{(e)}} = \left[\frac{(2\alpha/\theta)^2}{\zeta}\right]\left\{\int_0^{2\alpha}\frac{\sinh\phi(t)}{t}[K_0(t) - GI_0(t)]\,\mathrm{d}t\right\} \tag{38}$$

$$\lambda^{(c)} \equiv \frac{U_P^{(c)}}{U_0^{(c)}} = \left[-\frac{(2\alpha/\theta)^2}{2\ln(1-\gamma^2)}\right]\left\{\int_0^{2\alpha} \frac{[\cosh\phi(t)-1]}{t} \times [K_0(t) - GI_0(t)]\,\mathrm{d}t\right\} \quad (39)$$

Since $\lambda^{(c)}$ and $\lambda^{(e)}$ are the *weighting factors* by which the chemiphoretic and electrophoretic contributions of the diffusiophoretic velocity of a *bare* colloidal particle are altered due to polymer adsorption, one can rewrite eq 35 as

$$U_P = \lambda^{(e)}U_0^{(e)} + \lambda^{(c)}U_0^{(c)} \quad (40)$$

It is clear from eq 40 that it is sufficient to study the dependence of the weighting factors, $\lambda^{(c)}$ and $\lambda^{(e)}$, upon the parameters determining the structure of the adsorbed polymer layer to understand the role of the latter on U_P. In this regard, it is important to note that $\lambda^{(c)}$ and $\lambda^{(e)}$ are independent of β and the magnitude of the electrolyte gradient. In addition, as will be shown below, for the case of adsorption of an uncharged polymer, $\lambda^{(c)}$ and $\lambda^{(e)}$ are insensitive to the sign of ζ (the zeta potential of the colloidal particle) as well and assume positive values lying between zero and unity. However, for polyelectrolyte adsorption, $\lambda^{(c)}$ and $\lambda^{(e)}$ will exhibit a more complex behavior. Finally, it is interesting to note that $\lambda^{(e)}$ has the following additional significance: it also represents the factor by which the *electrophoretic mobility* of a colloidal particle is modified due to polymer adsorption.

Inasmuch as our objective is to focus on the role of the adsorbed polymer layer, defining a *reduced total* diffusiophoretic velocity of the particle with adsorbed polymer, $\bar{U}_P$, further facilitates the analysis:

$$\bar{U}_P \equiv U_P/U_0 \quad (41)$$

Clearly, the sign and magnitude of $\bar{U}_P$ denote (respectively) the direction and magnitude of the speed of the particle with adsorbed polymer *relative* to its speed when there is no polymer. $\bar{U}_P$, when expressed in terms of $\lambda^{(c)}$ and $\lambda^{(e)}$, has the form

$$\bar{U}_P = \lambda^{(c)}\bar{U}_0^{(c)} + \lambda^{(e)}\bar{U}_0^{(e)} \quad (42)$$

where

$$\bar{U}_0^{(c)} \equiv U_0^{(c)}/U_0 \qquad \bar{U}_0^{(e)} \equiv U_0^{(e)}/U_0$$

$\bar{U}_0^{(c)}$ and $\bar{U}_0^{(e)}$, which denote the *reduced* contributions of chemiphoresis and electrophoresis to the total diffusiophoretic velocity of a *bare* colloidal particle (U_0) can be written, by using eqs 14, 15, and 16b, as

$$\bar{U}_0^{(e)} = \frac{\beta\bar{\zeta}}{[\beta\bar{\zeta} - 2\ln(1-\gamma^2)]} \quad (43)$$

$$\bar{U}_0^{(c)} = \frac{-2\ln(1-\gamma^2)}{[\beta\bar{\zeta} - 2\ln(1-\gamma^2)]} \quad (44)$$

Equations 43 and 44, in addition to providing the relative magnitudes of chemiphoresis and electrophoresis to the total velocity of a bare colloidal particle, explicitly bring out the fact that $\bar{U}_0^{(c)}$ and $\bar{U}_0^{(e)}$ oppose each other when the two parameters β and $\bar{\zeta}$ have opposite signs.

In the next section we will discuss the results obtained for uncharged as well as charged polymers. All the results are presented in terms of $\bar{U}_P$ and its components $\lambda^{(c)}$ and $\lambda^{(e)}$.

3. Results and Discussion

3.1. Uncharged Adsorbed Polymers. Expressions for the Weighting Factors $\lambda^{(c)}$ and $\lambda^{(e)}$. Since the polymer is uncharged, the term containing the parameter A in eq 25 will be equal to zero and the solution of the equation that remains will simply be eq 10 as mentioned before. Equation 10 can be rewritten in terms of the transformation variable t, and the resulting equation can be used to express the hyperbolic trigonometric functions of ϕ appearing on the right-hand side of eqs 38 and 39 as explicit functions of t, to obtain

$$\lambda^{(e)} = \left[\frac{(4\alpha/\theta)^2\gamma}{(2\alpha)^{2\alpha/\theta}\bar{\zeta}}\right]\left\{\int_0^{2\alpha}\left[\frac{t^{(2\alpha/\theta)-1}\left[1+\gamma^2\left(\frac{t}{2\alpha}\right)^{4\alpha/\theta}\right]}{\left[1-\gamma^2\left(\frac{t}{2\alpha}\right)^{4\alpha/\theta}\right]^2}\right] \times [K_0(t) - GI_0(t)]\,\mathrm{d}t\right\} \quad (45)$$

and

$$\lambda^{(c)} = \left[-\frac{(4\alpha/\theta)^2\gamma^2}{(2\alpha)^{4\alpha/\theta}\ln(1-\gamma^2)}\right]\left\{\int_0^{2\alpha}\frac{t^{(4\alpha/\theta)-1}}{\left[1-\gamma^2\left(\frac{t}{2\alpha}\right)^{4\alpha/\theta}\right]^2} \times [K_0(t) - GI_0(t)]\,\mathrm{d}t\right\} \quad (46)$$

One can easily compute $\lambda^{(c)}$ and $\lambda^{(e)}$ from the above equations using a simple numerical integration procedure. The functions $I_0(t)$ and $K_0(t)$ in these equations can be evaluated by using, respectively, the IMSL routines BSIO and BSKO whereas the integration can be performed by using the IMSL routine QDAGS, which employs the Gauss–Kronrod rule.

The three important parameters upon which $\lambda^{(c)}$ and $\lambda^{(e)}$ depend are (i) θ, which, as noted earlier, is the ratio of the debye length to the characteristic length l defined in eq 30b, (ii) the "shielding ratio" α [$=(b/l)$], and (iii) the dimensionless zeta potential of the colloidal particle $\bar{\zeta}$. It may, however, be verified from eqs 45 and 46 that the sign of either $\lambda^{(c)}$ or $\lambda^{(e)}$ does not depend on the sign of the ζ potential of the colloidal particle—remember that γ has the same sign as $\bar{\zeta}$. In all our computations θ is assigned values ranging from 0 to 2, α is assigned a value of 3.42 (which is based on some typical values of b, η, ρ_P^0 and f provided by Varoqui and Dejardin[4]), and $|\bar{\zeta}|$ is allowed to vary from 0 to 14.

While all the computations of this subsection are carried out for surfaces of constant $\bar{\zeta}$, it should be noted that the expressions derived for $\lambda^{(i)}$ and $\bar{U}_P$ (eqs 45, 46, and 42) are also valid for the case in which the surface charge density, σ, of the particle is specified. The required $\bar{\zeta}$ value for this later case can be determined by using eq 19. This is so because it is assumed in the foregoing analysis that the adsorption of uncharged polymer will not alter the structure of the electrical double layer.

The variation of $\lambda^{(c)}$ and $\lambda^{(e)}$ with the ratio α/θ and $|\bar{\zeta}|$, at a fixed α value of 3.42, is plotted in Figures 2 and 3, respectively. Parts a and b of Figure 2 display $\lambda^{(c)}$ and $\lambda^{(e)}$ vs α/θ, respectively, for three different values of $|\bar{\zeta}|$ while parts a and b of Figure 3 display $\lambda^{(c)}$ and $\lambda^{(e)}$ vs $|\bar{\zeta}|$ for three different values of θ. These figures reveal that (i) $\lambda^{(c)}$ and $\lambda^{(e)}$ always assume positive values lying between zero and unity, (ii) for any given set of values of α, θ, and $|\bar{\zeta}|$, $\lambda^{(c)}$ is always much smaller than $\lambda^{(e)}$, (iii) both $\lambda^{(c)}$ and $\lambda^{(e)}$ decrease exponentially as α/θ is raised, and $\lambda^{(c)}$ does so more rapidly than $\lambda^{(e)}$, and (iv) at any given α/θ, both $\lambda^{(c)}$ and $\lambda^{(e)}$ increase as $\bar{\zeta}$ is decreased and reach asymptotic

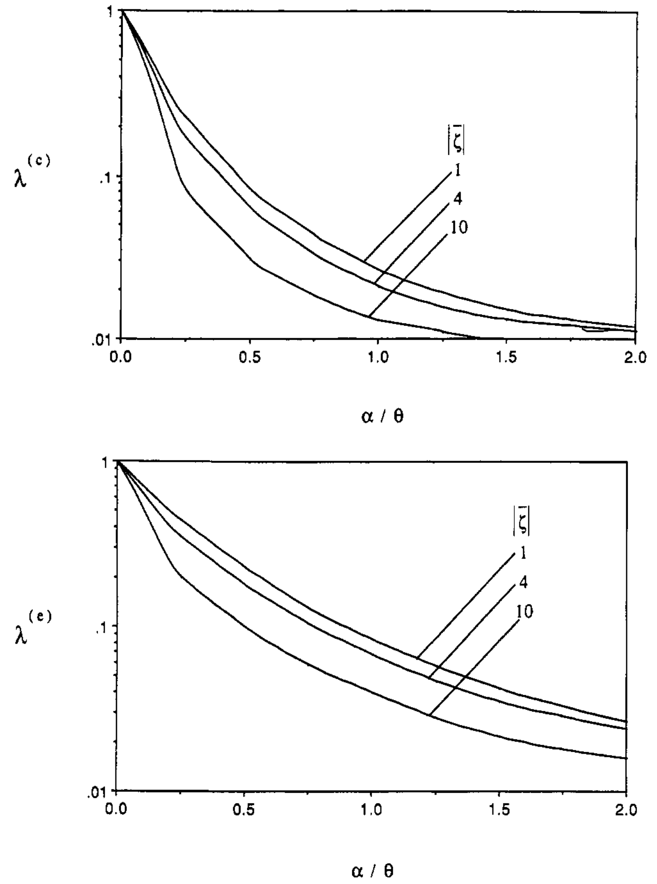

Figure 2. (a and b) Variation of the weighting factors, $\lambda^{(c)}$ and $\lambda^{(e)}$, with the ratio α/θ for an uncharged polymer at a fixed value of α (=3.42) and for different values of $|\bar\zeta|$. Note that the ratio α/θ is the ratio of b (the characteristic distance to which the segments of the adsorbed polymer molecules extend into the solution) to κ^{-1} (the debye length). Changing the ratio α/θ at a fixed value of α is, therefore, equivalent to varying the ionic strength of the medium.

limiting values, independent of $\bar\zeta$, at very low values of $\bar\zeta$ (Figure 3).

First of all, it is not surprising that the computations indicate $0 \leq \lambda^{(c)}, \lambda^{(e)} \leq 1$, because when the adsorbed polymer is uncharged, the only role of its segments is to impart an extra resistance to the flow of fluid past the colloidal particle. Thus, both chemi- and electrophoretic components are reduced due to the adsorption of an uncharged polymer, though to different extents. The observed larger extent of reduction of the chemiphoretic component compared to the electrophoretic component is a result of the fact that the polymer segments in the regions far removed from the particle's surface contribute chiefly to the overall drag offered by the adsorbed polymer.[5] The extent to which each of the velocity components is affected by the polymer is governed by the magnitude, in the region far-removed from the particle's surface, of the force responsible for its existence. The two forces responsible for the existence of chemi- and electrophoretic components are the first and second terms on the right-hand side of eq 24, respectively. In the absence of an externally applied electric field, the magnitudes of cosh $\phi - 1$ and sinh ϕ determine the magnitude of the two forces, respectively. Since cosh $\phi - 1 \sim \phi^2/2$ and sinh $\phi \sim \phi$ in the outer regions of the diffuse layer, the magnitude of the force responsible for electrophoresis is larger than the force responsible for chemiphoresis in regions far-removed from the particle surface. This larger driving force of electrophoresis when balanced by the drag due to polymer segments and viscous stresses leads to $\lambda^{(e)}$ values greater than $\lambda^{(c)}$.

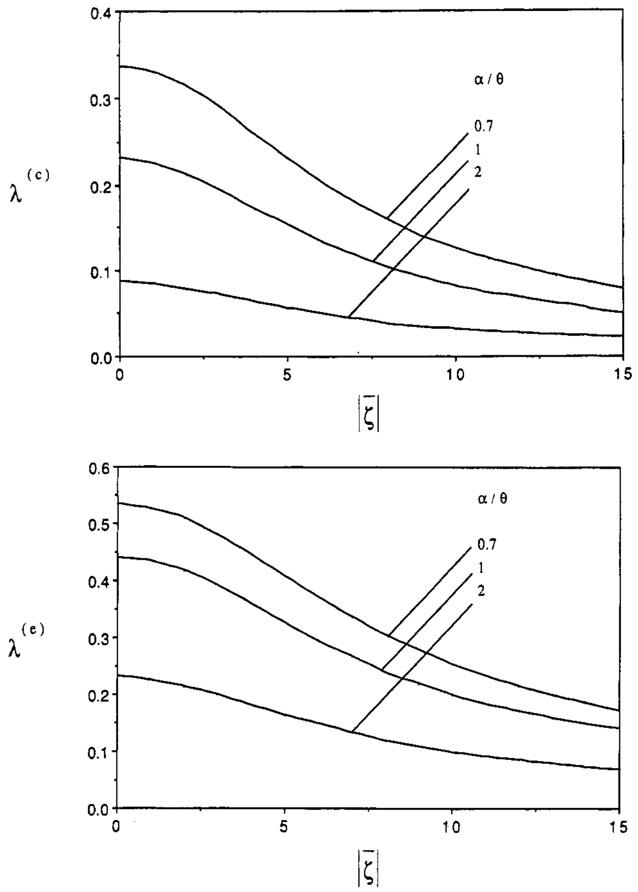

Figure 3. (a and b) Variation of the weighting factors, $\lambda^{(c)}$ and $\lambda^{(e)}$, with $|\bar\zeta|$ for an uncharged polymer at a fixed value of the shielding ratio α (=3.42) and for different values of the ratio α/θ.

Since the ratio α/θ equals b/κ^{-1} and since α was held fixed in our computations, varying the ratio α/θ in Figure 2 is equivalent to varying the debye length (or the ionic strength of the medium). When α/θ is small, the distance over which the adsorbed polymer's segments extend into the fluid is much smaller compared to the distance to which the diffuse charge layer of mobile ions pervades into the solution ($b \ll \kappa^{-1}$). As a result, the majority of the fluid elements within the diffuse layer are not subjected to the hydrodynamic drag of the polymer segments during their motion. Therefore, at very low values of α/θ the fractional reduction of the chemiphoretic and electrophoretic velocity components by the adsorbed polymer is not so high. However, as the ionic strength is raised, the diffuse layer gets gradually compressed, bringing a progressively higher fraction of the fluid elements of the diffuse layer into the spatial region occupied by the polymer segments, thus subjecting these elements to the extra drag of these segments. Consequently, both $\lambda^{(c)}$ and $\lambda^{(e)}$ decrease exponentially as the ionic strength is raised as seen in Figure 2. The fact that $\lambda^{(c)}$ decreases more rapidly than $\lambda^{(e)}$ as the ionic strength is raised is, once again, related to the fact that a given variation in ionic strength leads to unequal variation in the two driving forces responsible for the existence of each of the two velocity components.

In order to understand the observed variation of $\lambda^{(c)}$ (or $\lambda^{(e)}$) with $\bar\zeta$, it helps to examine the limiting behavior of these quantities at very small and very large values of $\bar\zeta$. One can easily deduce from eqs 45 and 46 the following asymptotic expressions for $\lambda^{(c)}$ and $\lambda^{(e)}$ in the limit of small and large $\bar{\zeta}$ with the help of eq 17:

$$\lambda^{(e)} = \left[\frac{(2\alpha/\theta)^2}{(2\alpha)^{2\alpha/\theta}}\right]\left\{\int_0^{2\alpha} t^{(2\alpha/\theta)-1}[K_0(t) - GI_0(t)]\,\mathrm{d}t\right\} \quad \text{for } |\bar{\zeta}|/4 \ll 1 \quad (45a)$$

$$\lambda^{(e)} = \left[\frac{(4\alpha/\theta)^2}{(2\alpha)^{2\alpha/\theta}|\bar{\zeta}|}\right]\left\{\int_0^{2\alpha}\left[\frac{t^{(2\alpha/\theta)-1}\left[1 + \left(\frac{t}{2\alpha}\right)^{4\alpha/\theta}\right]}{\left[1 - \left(\frac{t}{2\alpha}\right)^{4\alpha/\theta}\right]^2}\right][K_0(t) - GI_0(t)]\,\mathrm{d}t\right\} \quad \text{for } |\bar{\zeta}|/4 \gg 1 \quad (45b)$$

$$\lambda^{(c)} = \left[\frac{(4\alpha/\theta)^2}{(2\alpha)^{4\alpha/\theta}}\right]\left\{\int_0^{2\alpha} t^{(4\alpha/\theta)-1}[K_0(t) - GI_0(t)]\,\mathrm{d}t\right\} \quad \text{for } |\bar{\zeta}|/4 \ll 1 \quad (46a)$$

$$\lambda^{(c)} = \left[\frac{2(4\alpha/\theta)^2}{(2\alpha)^{4\alpha/\theta}|\bar{\zeta}|}\right]\left\{\int_0^{2\alpha}\frac{t^{(4\alpha/\theta)-1}}{\left[1 - \left(\frac{t}{2\alpha}\right)^{4\alpha/\theta}\right]^2}[K_0(t) - GI_0(t)]\,\mathrm{d}t\right\} \quad \text{for } |\bar{\zeta}|/4 \gg 1 \quad (46b)$$

Equations 45a and 46a show that $\lambda^{(c)}$ and $\lambda^{(e)}$ are independent of $\bar{\zeta}$ for low values of $|\bar{\zeta}|$ while eqs 45b and 46b reveal that these quantities are inversely proportional to $|\bar{\zeta}|$ for large values of $|\bar{\zeta}|$—two conclusions that are in agreement with the observations made in Figure 3.

As was pointed out earlier, $\lambda^{(e)}$ is also the factor by which the electrophoretic mobility of a colloidal particle is altered due to polymer adsorption. Recently, Varoqui had developed a series solution for $\lambda^{(e)}$ valid for $|\bar{\zeta}| \ll 1$.[37] His model, as ours, is also based on an exponential decay of polymer segment concentration from the adsorbing plane. A quantitative comparison of the predictions of our limiting equation corresponding to $|\bar{\zeta}|/4 \ll 1$ (eq 45a) with Varoqui's series solution (Figures 2 and 3 of ref 37) reveals a perfect agreement between the two, thus attesting to the correctness of the more general expression for $\lambda^{(e)}$ developed here. As noted in the Introduction, another parameter that is often employed in characterizing the effect of adsorbed polymer on the electrophoretic mobility of a colloidal particle is the so-called "electrokinetic thickness", δ_e.[1] It is, then, interesting to see how $\lambda^{(e)}$ is related to δ_e.

Relation between $\lambda^{(e)}$ and Electrokinetic Thickness. δ_e is defined as the distance by which, in the absence of adsorbed polymer, the "surface of shear" needs to be shifted (from its actual location) to reduce the particle's electrophoretic velocity to the same extent as does the adsorbed polymer.[1] If one denotes the (dimensionless) electrostatic potential at this new location of the surface of shear by $\bar{\zeta}_{\mathrm{app}}$, it follows from eq 16a that

$$\lambda^{(e)} = (\bar{\zeta}_{\mathrm{app}}/\bar{\zeta}) \quad (47)$$

where $\bar{\zeta}$, as noted earlier, is the dimensionless zeta potential of the particle. Also, eq 6, which describes the electrical potential in the diffuse layer, provides the additional relation

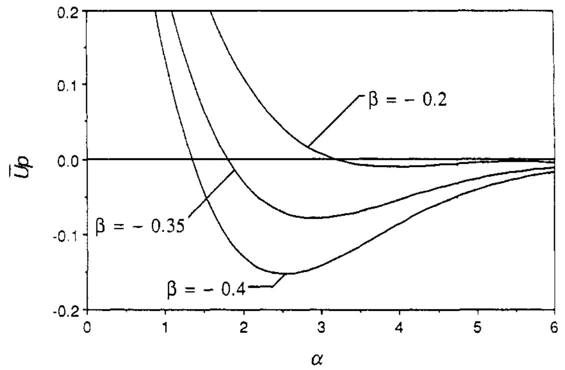

Figure 4. Reduced diffusiophoretic velocity, $\bar{U}_P$, of a colloidal particle with an adsorbed uncharged polymer vs the shielding ratio, α, for different values of the parameter β (the normalized difference in the diffusion coefficients of the two ions of the electrolyte; see eq 7). The values of the other parameters are $\bar{\zeta} = 6.0$ and $\theta = 4.74$.

$$\tanh(\bar{\zeta}_{\mathrm{app}}/4) = \gamma e^{-\kappa\delta_e} \quad (48)$$

in which γ, as already defined, is equal to $\tanh(\bar{\zeta}/4)$. From eqs 47 and 48, one can write

$$\delta_e = \kappa^{-1}\ln\left(\frac{\gamma}{\tanh(\lambda^{(e)}\bar{\zeta}/4)}\right) \quad (49)$$

The above equation allows one to compute the electrokinetic thickness when once $\lambda^{(e)}$ is determined from eq 38.

Now, turning back to the main objective of the paper, we shall next examine what implications the above observed parametric dependence of $\lambda^{(c)}$ and $\lambda^{(e)}$ has on the diffusiophoretic velocity of the colloidal particle, U_P.

Implications to U_P. First of all, it may be recalled that for a bare colloidal particle (see the discussion following eq 18) the following apply:

(i) $U_0^{(c)}$ is negligible compared to $U_0^{(e)}$ for small values of $|\bar{\zeta}|$; the magnitude of these components becomes comparable for larger values of $|\bar{\zeta}|$, and for very large values of $|\bar{\zeta}|$ the particle migrates in the direction of $U_0^{(c)}$ (if $|\beta| < 1$).

(ii) $U_0^{(c)}$ and $U_0^{(e)}$ augment each other if the parameters β and $\bar{\zeta}$ have the same sign and oppose each other when β and $\bar{\zeta}$ have opposite signs.

Now, since U_P is obtained by linearly combining $U_0^{(c)}$ and $U_0^{(e)}$ after multiplication with weighting factors $\lambda^{(c)}$ and $\lambda^{(e)}$, which assume values of $0 \le \lambda^{(c)}, \lambda^{(e)} \le 1$, one can only expect a reduction in the total diffusiophoretic velocity of the particle when β and $\bar{\zeta}$ have the same sign (i.e., $0 \le \bar{U}_P \le 1$). However, in view of the fact that $\lambda^{(c)}$ is always much smaller than $\lambda^{(e)}$, a *reversal in the direction of migration of the particle* (i.e. a negative value for $\bar{U}_P$) becomes possible, when β and $\bar{\zeta}$ have opposite signs, over a range of values for these parameters in which $|U_0^{(c)}| > |U_0^{(e)}|$. As mentioned above, for very large $|\bar{\zeta}|$, $|U_0^{(c)}| > |U_0^{(e)}|$ if $|\beta| < 1$. Therefore, reversal of the particle velocity due to polymer adsorption can be expected at a fairly high value of $|\bar{\zeta}|$ when $|\beta| < 1$. Figure 4, where $\bar{U}_P$ is plotted against α (for $\bar{\zeta} = 6.0$, $\theta = 4.74$, and various values of β), shows clearly that, over a range of negative values of β, $\bar{U}_P$ does attain significant negative values. In fact, it can easily be deduced by using eqs 18, 45b, and 46b that for all α, θ, and β values satisfying the following inequality a reversal in the direction of migration can be expected provided $|\beta| <$

1 and $\bar{\zeta}/4 \gg 1$:

$$\int_0^{2\alpha} \frac{[K_0(t) - GI_0(t)]t^{(2\alpha/\theta)-1}}{\left[1 - \left(\frac{t}{2\alpha}\right)^{4\alpha/\theta}\right]^2} \left\{\left[1 + \left(\frac{t}{2\alpha}\right)^{4\alpha/\theta}\right] - 2\left(\frac{t}{2\alpha}\right)^{2\alpha/\theta}\right\} \mathrm{d}t > 0 \quad (50)$$

Finally, the fact that $\lambda^{(c)}$ is much smaller than $\lambda^{(e)}$ can make the chemiphoretic component negligibly small compared to the electrophoretic component even at fairly high values of $|\bar{\zeta}|$. This leads to the possibility that a colloidal particle, when there is adsorbed polymer on it, may not exhibit any appreciable diffusiophoresis at all with an electrolyte such as KCl, which has equal diffusion coefficients for its cation and anion, while being able to migrate, under identical conditions, in the solution of an electrolyte whose ions have unequal diffusion coefficients (e.g., NaCl). Indeed, Lin and Prieve observed during their experiments on diffusiophoresis that *sterically stabilized* colloidal suspensions did not undergo any observable migration in KCl gradients, while they did in NaCl gradients.[35]

3.2. Charged Adsorbed Polymer. In this subsection, we will assume that the polyelectrolyte is adsorbed on a colloidal particle of known surface charge density, σ, which is *fixed*. Since the plane of shear is at $y = 0$ (see Figure 1), the charge on the polyelectrolyte segments adsorbed as *trains* will *not* become a part of this surface charge density *but* will be a part of the spatially distributed charge that balances σ. Also, in this case, at a *given* ionic strength, the surface potential of the colloidal particle will be different when there is adsorbed polymer on it and when it is "clean". The surface potential of the bare particle, which we are denoting throughout the foregoing and the following analysis by the symbol $\bar{\zeta}$ is, as before, related to the surface charge density (σ) via eq 19. In order to determine the potential disdtribution around the particle in the presence of the polyelectrolyte, eq 25 has to be solved numerically for the boundary conditions given by eqs 26 and 27b. For the sake of computational convenience, we will first rewrite eq 25 (and its boundary conditions) in terms of the transformation variable t and then decompose the resulting equation into a system of two first-order differential equations by defining the following new variables

$$Y_1 = \phi(t) \qquad Y_2 = \mathrm{d}\phi/\mathrm{d}t$$

In terms of Y_1, Y_2, and t, eqs 25, 26, and 27b become

$$t^2(\mathrm{d}Y_2/\mathrm{d}t) + tY_2 = (2\alpha/\theta)^2 \sinh Y_1 - Bt^2 \quad (51)$$

where

$$B = 4\pi ZZ'e^2\eta/\epsilon kTf$$

$$\mathrm{d}Y_1/\mathrm{d}t = Y_2 \quad (52)$$

with

$$\text{at } t = 2\alpha, \quad Y_2 \equiv \Sigma = \left(\frac{4\pi Ze\sigma l}{\epsilon kT}\right) \quad (53)$$

$$\text{as } t \to 0, \quad Y_1 \to 0 \quad (54)$$

$\phi(t)$ (i.e., $Y_1(t)$) can be determined by solving eqs 51 and 52 *simultaneously* by using the IMSL routine BVPFD. The solution so obtained for the potential, $\phi(t)$, can be used to evaluate the functions cosh $\phi(t) - 1$ and sinh $\phi(t)$. Knowing these functions, one can compute from eqs 38 and 39 the weighting factors $\lambda^{(c)}$ and $\lambda^{(e)}$ using the same numerical quadrature scheme employed for the uncharged polymer case. Note that ϕ depends on four dimensionless parameters, α, θ, B, and Σ, characterizing, respectively, the distance to which the polyelectrolyte segments extend into the electrolyte solution, the ionic strength of the electrolyte solution, the degree of dissociation of the polyelectrolyte, and the intrinsic fixed charge density of the colloidal particle.

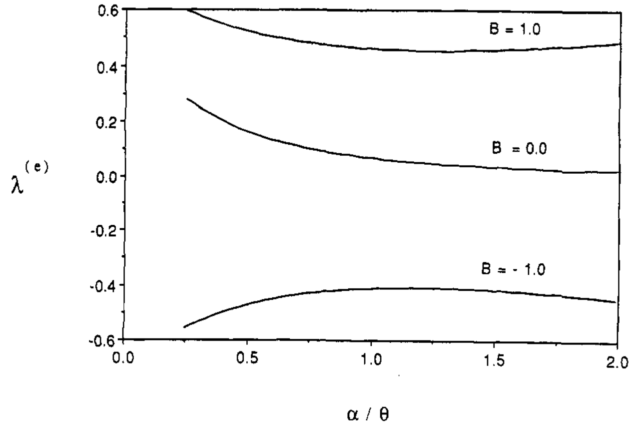

Figure 5. $\lambda^{(e)}$ vs α/θ for the case of polyelectrolyte adsorption for different values of the parameter B and for fixed values of α (=3.42) and Σ (=2.0). The parameter B determines the average charge, Z', per segment of the polyelectrolyte (see eq 51). The B values in the figure correspond to Z' values ranging from +0.3 to −0.3, when the other constants appearing in the definition of B are assigned the following values: $k = 1.38 \times 10^{-16}$ ergs molecule^{-1} K^{-1}; $T = 298$ K; $\epsilon = 78.54$; $e = 4.8 \times 10^{-10}$ esu; $Z = 1$, and $(f/\eta) = 25$ Å. Similarly, the value of Σ employed corresponds to a σ of +0.5 μC/cm^2, when the characteristic length l is assigned a typical value of 5.57 Å^4 (see eq 53).

Our computations reveal that (i) the sign, magnitude, and spatial variation of the electrostatic potential $\phi(t)$ in the region surrounding the particle are determined mainly by the sign and magnitude of the charge on the polyelectrolyte, except at very low degrees of ionization of the polyelectrolyte, and (ii) the intrinsic surface charge density (σ) of the particle has a very modest influence on $\phi(t)$ at all but very low extents of ionization of the adsorbed polymer.

A closer inspection of eqs 38 and 39 in light of the above two observations indicates that at all but very low degrees of ionization of the polyelectrolyte (i) $\lambda^{(e)}$ shall assume negative values when the sign of σ is opposite to that of the charge on the polyelectrolyte and (ii) $\lambda^{(c)}$ shall always be positive irrespective of the sign of the charge on the particle or the polymer. These conclusions follow from the fact that the functions sinh $\phi(t)$ and cosh $\phi(t) - 1$ appearing in eqs 38 and 39 are odd and even functions of ϕ, respectively. Indeed, Figures 5 and 6 where $\lambda^{(e)}$ and $\lambda^{(c)}$ are plotted against the ratio α/θ for $\Sigma = +2$ and $\alpha = 3.42$ and for various values of the parameter B display the expected trends. Figures 5 and 6 further show that the magnitudes of both $\lambda^{(e)}$ and $\lambda^{(c)}$ increase as the degree of ionization of the polyelectrolyte increases.

High degrees of polyelectrolyte charging would lead to quantitative deviation from the assumed exponential decay for SDD. Therefore, computations in Figures 5 and 6 were restricted to low degrees of dissociation. However, computations performed with our model for higher degrees of charging indicate that as the ionization of the polyelectrolyte increases (i) the magnitudes of $\lambda^{(c)}$ and $\lambda^{(e)}$ can become greater than unity and (ii) $\lambda^{(c)}$ becomes progressively less sensitive to the sign of the fixed charges of the polyelectrolyte. The invalidity of exponential decay for SDD at higher degress of polyelectrolyte charging renders these results only qualitative. However, we believe that the these results are insensitive to the actual con-

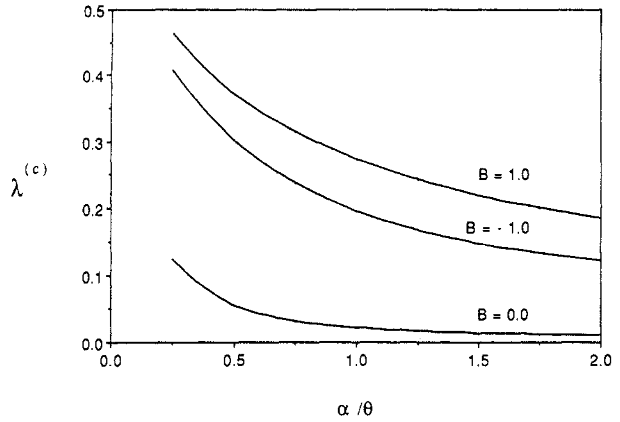

Figure 6. $\lambda^{(c)}$ vs α/θ for the case of polyelectrolyte adsorption for the same parameter values used in Figure 5.

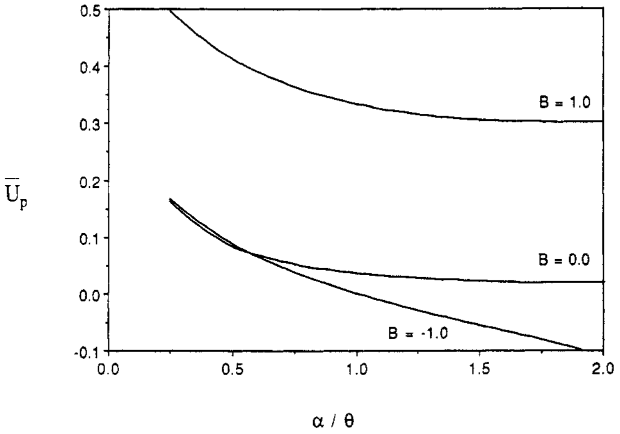

Figure 7. $\bar{U}_P$ vs α/θ for the case of polyelectrolyte adsorption for the same parameter values used in Figure 5 and $\beta = +0.2$.

formational details for the following reason. When the degree of ionization of the polyelectrolyte is small, the total distributed charge on the polyelectrolyte is smaller than or comparable in magnitude to the intrinsic fixed charge density, σ, of the particle. Hence, the magnitude of $\phi(t)$ is sensitive to the algebraic sum of σ and the total charge due to the polyelectrolyte segments. However, irrespective of the actual conformational details, at higher degrees of ionization of the polyelectrolyte, its charge far outweighs σ, and hence the spatial variation of ϕ is essentially controlled by the polymer charge. This, in our opinion, leads to the above results. Quantitative computations using the more rigorous theories of polyelectrolyte adsorption[31,32] can be used to confirm these facts.

The observed behavior of $\lambda^{(c)}$ and $\lambda^{(e)}$, in turn, has interesting implications to the diffusiophoretic velocity of the particles. In Figures 7 and 8, we examine the effect of the adsorbed polyelectrolyte on $\bar{U}_P$ for the two cases in which the β and Σ (or equivalently $\bar{\zeta}$) have the same sign and opposite sign, respectively. In Figure 7 we plot $\bar{U}_P$ vs α/θ for a particle suspended in an electrolyte with a β of +0.2 and Σ of +2. Figure 8 is a similar plot in which all the parameters are the same as those in Figure 7 except β, which is now −0.2 instead of +0.2. The value used for α in both the figures is the same as that in Figures 5 and 6. These figures show that polyelectrolyte adsorption, under appropriate conditions, could lead to particle migration speeds that are higher than those obtained in the absence of polymer adsorption (i.e., $\bar{U}_P > 1$; see Figure 8) and a reversal in the direction of particle migration (i.e., negative values of $\bar{U}_P$) as the ionic strength of the medium is changed.

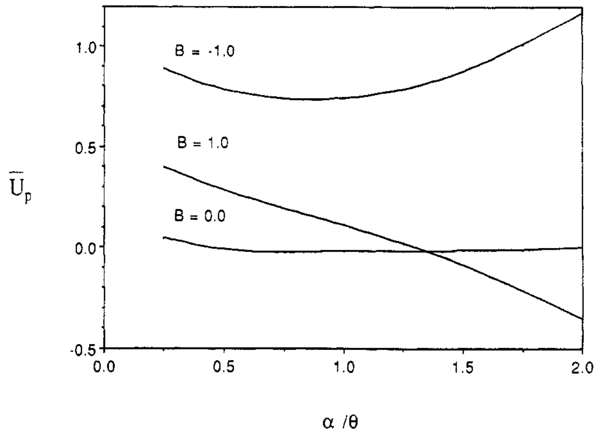

Figure 8. $\bar{U}_P$ vs α/θ for the case of polyelectrolyte adsorption for the same parameter values used in Figure 5 and $\beta = -0.2$.

4. Conclusions

This paper attempts to throw light upon the changes that occur in the diffusiophoretic velocity as well as the electrophoretic mobility of charged colloidal particles when a polymer is adsorbed on their surface. Both uncharged and charged polymers (i.e., polyelectrolytes) have been considered and computations have been performed for some typical physically realizable situations. The adsorbed polymer is found to have a pronounced influence on the diffusiophoretic velocity of the particle. The adsorbed polymer is found to effect not only the magnitude of the diffusiophoretic velocity of the particle but also, in some cases, its direction of migration. When the adsorbed polymer is charged, the particle can, under certain conditions, acquire migration speeds that are much higher than those of clean particles. It appears that the diffusiophoretic velocities of particles of known surface charge characteristics can be manipulated by appropriately selecting the type of electrolyte, its concentration in the bulk solution, the type of polymer, and the degree of its adsorption on the surface of the particle. As mentioned earlier, this type of study of the effect of adsorbed polymers on the diffusiophoresis of charged colloids can provide a better insight into the conformations of the adsorbed polymer chains and can lead to better quantitative predictions for some types of cellular movement. The fact that the magnitude and, in some cases, the direction of the diffusiophoretic velocity of the particle can be altered by adsorbing polymers on its surface can, perhaps, be exploited to achieve separation of mixtures of colloidal particles by adsorbing polymers on them.

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