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Diffusiophoresis of a Spherical Particle Normal to a Plane

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Diffusiophoresis of a spherical colloidal particle normal to a plane subject to a uniform electrolyte concentration gradient is investigated theoretically for arbitrary double layer thickness and surface potential. The governing general electrokinetic equations are put in terms of bipolar spherical coordinates and solved numerically with a pseudospectral method based on Chebyshev polynomial. The effects of key parameters are examined such as the double layer thickness, surface potential, and the distance between the particle and the plane. It is found, among other things, that the presence of the boundary has a retardation effect on the motion of the particle, provided that the double layer does not touch the planar boundary. If it does, however, the velocity of the particle will exhibit a maximum as the double layer just loses touch of the plane, thanks to the competitive force of the polarization effect. The planar boundary poses not only as a conventional hydrodynamic retarding force, but also may distort the shape of the double layer greatly, hence altering its polarization situation, which has a profound electrostatic impact on the motion of the particle when it is close to the plane.

Introduction

Diffusiophoresis is the movement of a colloidal particle under the influence of a solute concentration gradient in the solution. The concept was first proposed by Deryagin and his co-workers^{1–4} and has been studied experimentally both in ionic^{3,5,6} and nonionic solutions.^{7,8} In a solution of uncharged solute, for example, small aerosol particles floating in the atmosphere,^{9,10} the solute molecules interact with the aerosol particles through the van der Waals and dipole forces. If the interaction between the solute molecules and the particle is attractive, the particle migrates toward the region of higher solute concentration, whereas the movement is toward lower solute concentration if the interacting force is repulsive. Many of the early theoretical and experimental studies on diffusiophoresis were on gaseous systems. Recent works, however, have started to focus on the diffusiophoresis in liquid systems involving charged colloidal particles suspended in electrolyte solutions. When a charged particle is immersed in an electrolyte solution, an induced electric force will arise when the concentration of electrolyte solute is somehow nonuniform in the solution. The terminology “diffusiophoresis” was first introduced by Deryagin and co-workers.^{1,4} Dukhin and Deryagin⁴ indicated that diffusiophoresis was caused by the polarization of the double layer under the influence of a bulk concentration gradient. The results of their theoretical analysis were verified both theoretically¹¹ and experimentally^{6,12} later. Meanwhile, Anderson et al.^{13,14} conducted a theoretical investigation of the diffusiophoresis of a spherical particle immersed in both the electrolyte and the nonelectrolyte solutions. They showed that the diffusiophoretic mobility in an electrolyte solution was determined essentially by three factors: the surface potential ζ on the particle surface, the dimensionless double layer thickness κa , and the relative diffusivity of ions [$\beta = (D_1 - D_2)/(D_1 + D_2)$], where D_1 and D_2 are respectively the diffusion coefficient of cations and

anions]. β is an experimentally measurable property of the specific electrolyte solution under consideration. For example, in an aqueous solution, β are respectively 0, -0.2 , and 0.64 for KCl, NaCl, and HCl.¹⁵ A negative value of β implies that the diffusion velocity of anions is greater than that of cations. Subsequently, a series of research efforts have been devoted to study the system of a single isolated hard particle with thin or thick double layer, at low or high zeta potentials.^{5,16,17} Baygents and Saville¹⁸ extended it further to consider the nonrigid particles such as a droplet or a small bubble immersed in an electrolyte solution. Misra et al.¹⁹ on the other hand extended it to the system of a single soft particle.

All of the above analyses were for a single particle, or equivalently, very dilute suspensions. As for the concentrated colloidal dispersions, Lee and his co-workers^{20,21} considered recently the diffusiophoresis of concentrated spherical particles with arbitrary double layer thickness and zeta potential suspended in electrolyte solutions. Keh and Wei^{22,23} meanwhile investigated the diffusiophoretic behavior for a concentrated suspension of spherical particles under the limitations of low zeta potential or very thin double layer thickness. They used both the Happel model²⁴ and the Kuwabara's unit cell model²⁵ to describe the system, with the conclusion that the performance of the latter is better.

One of the important factors to consider in analyzing the diffusiophoresis is the presence of a boundary. This factor needs to be considered in practical applications, for example, when a particle is sufficiently close to the capillary wall, such as condensation of small particles onto the condenser,²⁶ or the existence of neighboring particles can no longer be ignored if the concentration of a colloidal dispersion is relatively high.^{20–23} Another typical example is in permeable membranes where charged particles are driven by an applied concentration gradient.²⁷ Keh and Anderson²⁸ made a theoretical investigation on the boundary effects of a solid plane in electrophoresis originally. On the basis of this work, several studies were made on diffusiophoresis by Keh and co-workers^{29–31} later on for the

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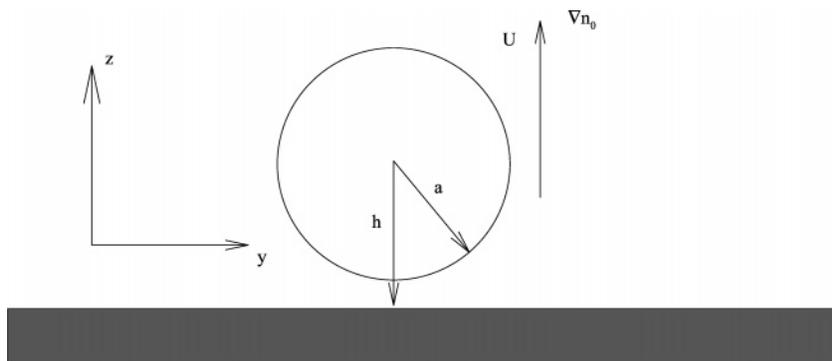


Figure 1. Schematic representation of the system under consideration where a is the radius of a particle and h is the distance between the center of the particle and the surface. The applied concentration gradient ∇n_0 is in the z direction.

cases of very thin double layer. According to their analyses, the diffusiophoretic velocity in an electrolyte solution does not vary monotonically with the separation distance any more as in electrophoresis when the so-called chemiphoretic and the electrophoretic effects become very profound.²⁹ Nevertheless, these results were restricted to special cases such as low surface potential or very thin double layer. The effects of double layer polarization and double layer overlapping are neglected in their analyses as a result. Their having to do this simplification is mainly due to the highly nonlinear nature of the governing electrokinetic equations, which makes solving them analytically almost impossible. Recently, Lee and co-workers^{32,33} established an efficient and reliable simulation algorithm to investigate the polarization effect on the electrophoretic motion of a spherical particle normal to a plane. They found that the hydrodynamic drag posed by the solid planar boundary and nonuniform distribution of double layer have a great influence on the movement of the colloidal particle under consideration. Moreover, a thorough investigation on diffusiophoresis made for concentrated colloidal suspensions by Lee and co-workers^{20,21} recently revealed that the diffusiophoretic velocity decreases with increasing volume fraction of colloidal particles. They showed that it is mainly due to the hindrance effect of neighboring particles as a hydrodynamic retardation force. Moreover, the higher the concentration of colloidal particles, the more significant the overlapping of the neighboring double layers, leading to a greater electrostatic interaction which reduces the driving force in the diffusiophoresis under consideration there. It also delays the dominance of polarization effect on the diffusiophoretic velocity as κa decreases.

In the present study, we consider the diffusiophoresis of a spherical colloidal particle normal to a solid plane subject to a uniform concentration gradient. The particle can have arbitrary surface potential and double layer thickness. This configuration is a classic one in the general studies of electrokinetic phenomena in colloid science regarding the effect of the presence of a boundary. It is of importance both in fundamental and in application aspects. For instance, it models the situation of a dilute dispersion of colloids near the solid wall of the container or the environment near a planar catalyst where the reaction takes place, consuming the electrolytes as participating reactants, thus establishing a concentration gradient. Our analysis presented here removes the previous restriction of a very thin double layer imposed by relative studies,²⁹ so that the polarization effect can be completely taken into account. A pseudospectral method based on Chebyshev polynomial is used to carry out the calculations. The effects of key factors, such as surface potential, double layer thickness, relative diffusion velocities between cations and anions, and the distance to the planar boundary are examined in detail.

Theory

Referring to Figure 1, we considered a charged spherical particle of radius a moves with velocity U normal to a planar surface in response to a uniformly applied concentration gradient, ∇n_0 , in the z direction. The distance between the center of the particle and the planar surface is h . An impervious planar metal surface is considered in this study, which is electrically grounded to the earth where the electric potential is taken to be zero. The desired concentration gradient ∇n_0 can be imposed, for example, by a chemical reaction on the planar surface which consumes electrolyte ions to some extent. A representative case can be found in the experimental work by Smith and Prieve.¹² The dispersion liquid contains $z_1:z_2$ electrolytes, z_1 and z_2 are respectively the valences of cations and anions. The electro-neutrality constraint in the bulk liquid phase requires that $n_{20} = n_{10}/\alpha$, where n_{10} and n_{20} are the bulk concentrations of cations and anions, respectively, and $\alpha = -z_2/z_1$. The bipolar spherical coordinates (ξ, η, φ) are adopted where $\eta = 0$ and $\eta = \eta_0$ denotes respectively the planar wall and the particle–dispersion liquid interface. The bipolar coordinates and the Cartesian coordinates (x, y, z) are related by³⁴

$$z = c \frac{\sinh \eta}{\cosh \eta - \cos \xi} \quad (1)$$

$$y = c \frac{\sin \xi}{\cosh \eta - \cos \xi} \quad (2)$$

where c is the focal length, $0 \leq \eta < \eta_0$, and $0 \leq \xi \leq \pi$. It should be reminded that the radius of particle is always set to be a constant a with the variation of η_0 in convenience. Therefore, h can be defined in $a \cosh(\eta_0)$. The value of η_0 denotes the relative position between the particle and the planar boundary.

According to Dukhin and Semnikhin's analysis,³⁵ diffusiophoresis can be regarded as the electrophoresis caused by the microgradient of the electric potential induced by the concentration macrogradient. Thus, the same set of electrokinetic equations can be applied in either situation. Standard electrokinetic model is adopted in this analysis, which does not consider the additional surface conductivity caused by the surface current within a thin layer between the particle surface and the slipping plane.³⁶ The electric potential of the system under consideration, ϕ , is described by the Poisson equation:

$$\nabla^2 \phi = -\frac{\rho}{\epsilon} = -\sum_{j=1}^2 \frac{z_j e n_j}{\epsilon} \quad (3)$$

where ρ and ϵ are respectively the space charge density and the permittivity of the solution; e is the elementary charge, and n_j and z_j respectively are the number concentration and the valence of ionic species j , where $j = 1$ would be cations and $j = 2$ would be anions. Moreover, the flow field is governed by the Stokes equation, with a modification to include the electric body force, as well as the incompressibility constraint:

$$\mu \nabla^2 \mathbf{v} - \nabla p - \rho \nabla \phi = 0 \quad (4)$$

$$\nabla \cdot \mathbf{v} = 0 \quad (5)$$

where p and μ are respectively the pressure and the viscosity of the fluid. It is assumed that the physical properties of the electrolyte solution take their macroscopic values. Also, the shape of the colloidal particle remains spherical when migrating in the fluid, which is true for low Reynolds number in the creeping flow regions. The ionic concentration n_j is governed by the conservation of ion species:

$$\frac{\partial n_j}{\partial t} = -\nabla \cdot \mathbf{f}_j \quad (6)$$

$$\mathbf{f}_j = -D_j \left(\nabla n_j + \frac{n_j z_j}{kT} \nabla \phi \right) + n_j \mathbf{v} \quad (7)$$

where \mathbf{f}_j represents ionic flux of ion species j , D_j is the diffusion coefficient for ion j , and z_j is the valence for ion j . When the motion of the charged particle is at steady state, eqs 6 and 7 can be combined as

$$\frac{kT}{D_j} \left[\nabla^2 n_j + \frac{z_j e}{kT} (\nabla n_j \cdot \nabla \phi + n_j \nabla^2 \phi) \right] - \nabla n_j \cdot \mathbf{v} = 0 \quad (8)$$

The ion distribution in the electrolyte solution is assumed to take the following form similar to the Boltzmann distribution:

$$n_j = n_{j0} \exp \left(-\frac{z_j e}{k_B T} (\phi_e + \delta \phi + g_j) \right) \quad (9)$$

where n_{j0} is the bulk concentration of the species j . In order to account for possible concentration polarization arising from the movement of particle in the present problem, the electrical potential ϕ is decomposed into ϕ_e and $\delta \phi$. The former represents the equilibrium electrical potential in the corresponding static problem, and the latter denotes the difference of ϕ and ϕ_e . Following the same treatment as employed in the classic work by O'Brien and White,³⁷ an additional perturbed potential g_j is used to take into account the convection contribution to the ion flux, the so-called polarization effect. It is further assumed that the concentration of solute is only slightly nonuniform over the length scale a ; that is, $a|\nabla \mathbf{n}_0| \ll n_0$. Therefore, the potential perturbation arising from the applied concentration gradient is negligible in comparison with the surface charges on the particle. As $\delta \phi$ and g_j are small compared with both $k_B T/e$ and ϕ_e , eq 9 can be further simplified as

$$n_j = n_{j0} \exp \left(-\frac{z_j e}{k_B T} \phi_e \right) \left[1 - \frac{z_j e}{k_B T} (\delta \phi + g_j) \right] \quad (10)$$

After substituting eq 10 into eqs 3, 5, and 8, we can further convert them to dimensional form with the following replacements: $\phi_e^* = \phi_e/\zeta$, $\delta \phi^* = \delta \phi/\zeta$, $g_j^* = g_j/\zeta$, and $n_j^* = n_j/n_{10}$, where ζ represents the surface potential on the shear plane. The electrokinetic equations can be linearized by neglecting the terms that involve products of small quantities such as $\delta \phi$ and g_j . After

some mathematical manipulations, the equilibrium potential is governed by

$$\nabla^{*2} \phi_e^* = -\frac{(\kappa a)^2}{(1 + \alpha)\phi_r} [\exp(-\phi_r \phi_e^*) - \exp(\alpha \phi_r \phi_e^*)] \quad (11)$$

where the inverse Debye length κ and the scaled zeta potential ϕ_r are defined respectively by

$$\kappa = \left[\sum_{j=1}^2 n_{j0} (e z_j)^2 / \epsilon k_B T \right]^{1/2} \quad (12)$$

$$\phi_r = \frac{\zeta}{kT/z_1 e} \quad (13)$$

$$\nabla^{*2} = \frac{x^2}{c^*} \left(\frac{\partial^2}{\partial \eta^2} + \frac{\partial^2}{\partial \xi^2} - \frac{\sinh \eta}{x} \frac{\partial}{\partial \eta} + \frac{\cos \xi \cosh \eta - 1}{x \sin \xi} \frac{\partial}{\partial \xi} \right) \quad (14)$$

In these expressions, $c^* = c/a$, and $x = \cosh \eta - \cos \xi$. Since the surface potential of particle remains constant and the impervious metal surface is electrically grounded to the earth, the boundary conditions for ϕ_e^* are respectively

$$\phi_e^* = 1 \quad \text{at } \eta = \eta_0 \quad (15)$$

$$\phi_e^* = 0 \quad \text{at } \eta = 0 \quad (16)$$

$$\frac{\partial \phi_e^*}{\partial \xi} = 0 \quad \xi = 0, \pi \quad (17)$$

Equation 17 implies the symmetric nature of the problem.

Introducing stream function and taking curl of eq 4, the flow field can be obtained as

$$E^{*4} \psi^* = -(\kappa a)^2 \frac{\sin \xi}{c^*} \left(\frac{\partial \phi_e^*}{\partial \xi} \frac{\partial \delta \phi^*}{\partial \eta} - \frac{\partial \phi_e^*}{\partial \eta} \frac{\partial \delta \phi^*}{\partial \xi} \right) \quad (18)$$

where ψ^* is the scaled stream function, E^{*4} is the operator of $E^{*2} E^{*2}$, which is defined as

$$E^{*2} = \frac{x^2}{c^{*2}} \left(\frac{\partial^2}{\partial \eta^2} + \frac{\partial^2}{\partial \xi^2} + \frac{\sinh \eta}{x} \frac{\partial}{\partial \eta} + \frac{1 - \cos \xi \cosh \eta}{x \sin \xi} \frac{\partial}{\partial \xi} \right) \quad (19)$$

and the associated boundary conditions are

$$\psi^* = -\frac{1}{2} \left(\frac{c^* \sin \xi}{x} \right)^2 U^* \quad \text{at } \eta = \eta_0 \quad (20)$$

$$\frac{\partial \psi^*}{\partial \eta} = \frac{c^{*2}}{x^3} \sin \xi \sinh \eta U^* \quad \text{at } \eta = \eta_0 \quad (21)$$

$$\psi^* = 0 \quad \text{at } \eta = 0 \quad (22)$$

$$\frac{\partial \psi^*}{\partial \eta} = 0 \quad \text{at } \eta = 0 \quad (23)$$

$$\psi^* x = 0 \quad \text{at } \eta = 0 \text{ and } \xi = 0 \quad (24)$$

$$\psi^* = 0 \text{ and } \frac{\partial \psi^*}{\partial \xi} = 0 \quad \text{at } \xi = 0, \pi \quad (25)$$

Equations 20 and 21 indicate that the colloidal particle moves with a relative scaled velocity of U^* , and eqs 22–24 state that the fluid is stationary both on the plane and at infinity. Equation

25 implies that the velocity distribution is symmetric around the z direction.

Subtracting eq 3 from eq 11, one can get the governing equation of induced electrical potential in the dimensionless form:

$$\nabla^{*2}\delta\phi^* - \frac{(\kappa a)^2}{(1+\alpha)\phi_r}[\exp(-\phi_r\phi_e^*) + \alpha\exp(\alpha\phi_r\phi_e^*)]\delta\phi^* = \frac{(\kappa a)^2}{(1+\alpha)\phi_r}[\exp(-\phi_r\phi_e^*)g_1^* + \alpha\exp(\alpha\phi_r\phi_e^*)g_2^*] \quad (26)$$

Suppose that the net flux for cations and anions along the z direction is zero; that is,

$$(z_1\mathbf{f}_1 + z_2\mathbf{f}_2) \cdot \mathbf{z} = 0 \quad (27)$$

Substituting eq 7 into eq 27, we have

$$(\delta\phi^*) = -\frac{1}{\phi_r}\beta[(\nabla^*n_0^*) \cdot \mathbf{z}] \quad \text{at } \eta = 0 \quad (28)$$

$\nabla^*n_0^*$ refers to the dimensionless applied concentration gradient. Furthermore, since the particle under consideration is dielectric, we have

$$\frac{\partial\delta\phi^*}{\partial\eta} = 0 \quad \text{at } \eta = \eta_0 \quad (29)$$

And the symmetric nature of the problem yields

$$\frac{\partial\delta\phi^*}{\partial\xi} = 0 \quad \text{at } \xi = 0, \pi \quad (30)$$

The ion conservation equation is converted to the following form:

$$\nabla^{*2}g_j^* - \phi_r\nabla^*\phi_e^*\nabla^*g_j^* - \phi_r^2Pe_j\nabla^*(\nabla^*\phi_e^*) = 0 \quad j = 1, 2 \quad (31)$$

where $Pe_j = \epsilon(z_1e/k_B T)^2/\mu D_j$ is the Peclet number of ion j . Since the surface of particle is impervious, we have

$$\frac{\partial g_j^*}{\partial\eta} = 0 \quad \text{at } \eta = \eta_0 \quad (32)$$

And the symmetric nature of the problem requires that

$$\frac{\partial g_j^*}{\partial\xi} = 0 \quad \text{at } \xi = 0, \pi \quad (33)$$

An ionic concentration gradient in the z direction is imposed on the system, for example, by a chemical reaction involving electrolyte ions on the planar surface. Thus, we have

$$(\delta\phi^* + g_1^*) = -\frac{1}{\phi_r}[(\nabla^*n_0^*) \cdot \mathbf{z}], \text{ at } \eta = 0 \quad (34)$$

$$(\delta\phi^* + g_2^*) = \frac{1}{\alpha\phi_r}[(\nabla^*n_0^*) \cdot \mathbf{z}], \text{ at } \eta = 0 \quad (35)$$

The governing equations and the associated boundary conditions, eqs 11–35, are solved by a pseudospectral method based on Chebyshev polynomials. Details of this method can be found elsewhere.³⁸ It proves to be a very powerful and suitable method for the fields of interest such as electrophoresis, among other electrokinetic problems.

A force balance exerted on the particle is required for the convergence of numerical iteration. The expression of the electric force and the hydrodynamic force are shown as

$$F_{Ez}^* = 2\pi \int_0^\pi -\frac{\sin\xi}{x} \left(\frac{\partial\phi_e^*}{\partial\eta} + \frac{\partial\delta\phi}{\partial\eta} \right) \left[(1 - \cosh\eta \cos\xi) \left(\frac{\partial\phi_e^*}{\partial\eta} \right) - \sinh\eta \sin\xi \left(\frac{\partial\phi_e^*}{\partial\xi} \right) \right] d\xi \quad (36)$$

$$F_{Dz}^* = \pi \int_0^\pi \left[-\left(\frac{c^* \sin\xi}{x} \right) \frac{\partial}{\partial\eta} (E^{*2}\psi^*) - \frac{2c^* \sin\xi}{x^2} \sinh\eta (E^{*2}\psi^*) \right] d\xi - \frac{(\kappa a)^2}{(1+\alpha)\phi_r} \pi x \int_0^\pi \left(\frac{c^* \sin\xi}{x} \right)^2 \left(\frac{\partial\phi_e^*}{\partial\eta} + \frac{\partial\delta\phi}{\partial\eta} \right) \left\{ \exp(-\phi_r\phi_e^*) [1 - \phi_r(\delta\phi^* + g_1^*)] + \alpha \exp(\alpha\phi_r\phi_e^*) [1 + \alpha\phi_r(\delta\phi^* + g_2^*)] \right\} d\xi \quad (37)$$

where F_{Ez}^* and F_{Dz}^* are respectively the hydrodynamic force and the electric force acting on the particle.^{33,34} The velocity of the particle can be evaluated by the fact that the net force exerted on it vanishes at steady state; that is,

$$F_{Ez}^* + F_{Dz}^* = 0 \quad (38)$$

Note that since F_{Ez}^* and F_{Dz}^* are functions of electrical potential, electrolyte concentration distribution, and flow field, the computation of the scaled diffusiophoretic velocity involves an iterative procedure. The definition of the scaled diffusiophoretic mobility U_m^* is

$$U_m^* = \frac{U^*}{\nabla^*n_0^*} \quad (39)$$

For a specific applied concentration gradient $\nabla^*n_0^*$, an initial guess of U^* is used to start the iteration procedure and solve eqs 36 and 37. An updated U^* is then obtained by eq 39. This procedure continues until U^* satisfies eq 38.

Results and Discussion

Influence of Ionic Diffusion Velocity, $\beta = 0$ and $\beta \neq 0$.

For convenience, KCl ($Pe_1 = Pe_2 = 0.26$, and $\beta = 0$) and NaCl ($Pe_1 = 0.39$, $Pe_2 = 0.26$, and $\beta = -0.2$) are chosen as the representative cases of $\beta = 0$ and $\beta \neq 0$, respectively. They will be discussed separately as follows.

Referring to Figure 1, a uniform concentration gradient ∇n_0 is applied to the system in the z direction. Figure 2 shows the variation of the scaled diffusiophoretic velocity (U^*/U^0) normal to a solid plane as a function of the scaled surface potential ϕ_r at various values of κa , where $U^0 = (\epsilon/\mu a)(kT/z_1e)^2\nabla n_0$ is a reference diffusiophoretic velocity, which represents the velocity of a corresponding isolated sphere in an unbounded electrolyte solution with $\beta = 0$.¹⁴ The ϕ_r dependence of (U^*/U^0) turns out to be an even function for each κa . This behavior is similar to the observations in corresponding studies of diffusiophoresis of colloidal suspensions, dilute¹⁷ or concentrated.²⁰ It should be noted that, although the ionic diffusion velocities for cations and anions are identical, the counterions dominate in amount within the double layer. According to Dukhin's analysis,³⁹ the external concentration gradient induces an electrical dipole moment. Thus, accompanying the diffusion of counterions within the double layer, this induced electric field will set the particle in motion, whether $\beta = 0$ or $\beta \neq 0$.

Moreover, the scaled diffusiophoretic velocities exhibit local maxima as κa increases over 1.0. The larger the κa is (i.e., the

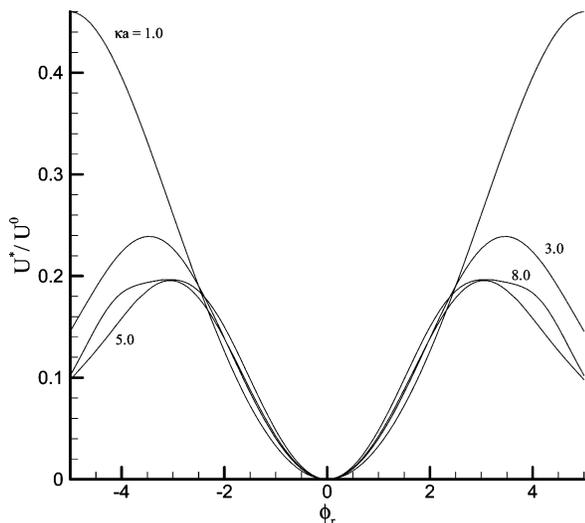


Figure 2. Variation of scaled diffusio-phoretic velocity (U^*/U^0) as a function of ϕ_r at various values of κa when $\eta = 1.0$, $\beta = 0$, and $\alpha = 1$.

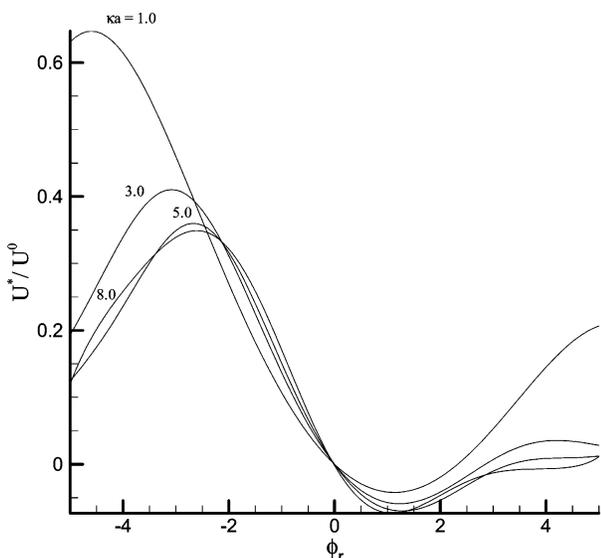


Figure 3. Variation of scaled diffusio-phoretic velocity (U^*/U^0) as a function of ϕ_r at various values of κa when $\eta = 1.0$, $\beta = -0.2$, and $\alpha = 1$.

thinner the double layer is), the smaller this maximum is. This is mainly due to the polarization effect of double layer, which has a tendency to retard the particle motion.^{20,33} This polarization effect will be elaborated in details again in subsequent sections.

However, as shown in Figure 3, the symmetric property of (U^*/U^0) with respect to ϕ_r no longer exists if the charged particle is in NaCl solution ($\beta \neq 0$). Moreover, when the scaled surface potential ϕ_r is roughly smaller than 2 and positive (U^*/U^0) becomes negative, as shown in Figure 3. This behavior was also reported by Prieve and Roman¹⁷ in their analysis of the behavior of an infinitely dilute dispersion, and it was commented briefly there that the behavior of diffusio-phoretic velocity is complicated when $\beta \neq 0$. Dukhin³⁹ pointed out that the diffusio-phoresis of a particle arises not only from chemi-phoretic effect but also electrophoretic effect. The electrophoretic effect is generated due to an induced electric field along the direction of the bulk concentration gradient since the diffusion velocity of cations is different from that of anions (i.e., $\beta \neq 0$). Because the diffusivity of chloride ion is larger than that of sodium ion, chloride ion has a stronger tendency to diffuse to the region of lower concentration, that is, more chloride ion will accumulate

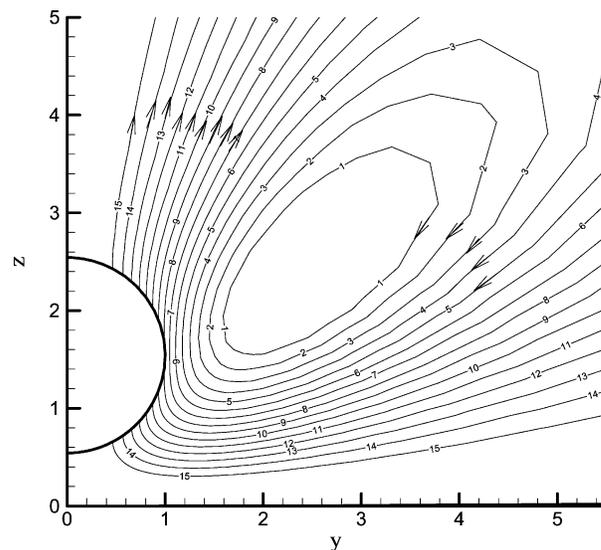


Figure 4. Contours of stream function ψ^* at $\beta = 0.0$, $\eta_0 = 1.0$, $\kappa a = 1.0$, $\phi_r = 2.0$, and $\alpha = 1$.

near the plane in NaCl solution than that in KCl solution. Besides, consider the extra contribution of Pe_j to the corresponding boundary conditions, distinct Pe_j tend to generate an additional driving force in general. This reflects in eq 28 in that an electric field arises in order to maintain the electroneutrality in the bulk phase. If the diffusivity of anions is larger than cations ($\beta < 0$ and $Pe_1 > Pe_2$) and the particle is positively charged, the induced electric field in eq 28 has an opposite direction to the applied concentration gradient. This additional driving force cannot be neglected unless the ionic diffusion velocities of cations and anions are identical, that is, $\beta = 0$.

From the above analysis, the induced electric field is directed toward the opposite direction of bulk concentration gradient. If the charged condition on the particle is negative ($\phi_r < 0$), the direction of the induced electric force will be the same as that of the original driving force provided by the applied concentration gradient. Comparing the magnitudes of the scaled velocities between Figure 2 and Figure 3, one can find that the negatively charged particle always moves faster in NaCl solution under the same κa and ϕ_r since it experiences an additional driving force due to the effect of distinct ionic diffusion velocity. Furthermore, the diffusio-phoretic behavior of a positively charged particle is much more complicated as the eventual velocity is determined by these two competing driving forces. If the induced electric field due to nonequivalent charge distribution has a greater influence than the bulk concentration gradient, the particle will move in the opposite direction. Malkin and Dukhin¹¹ first predicted the inversion of diffusio-phoresis direction, such as that seen in Figure 3 for $\phi_r > 0$, and later on, Dukhin³⁹ gave a detailed physical reasoning of this mechanism. Lee and co-workers²¹ also indicated that this induced electric field causes an electro-osmotic flow near the particle surface, which is observed here again with the presence of the planar boundary.

Further comparing the flow fields in Figures 4 and 5 respectively, we note that the particle will move in the opposite direction as $\beta \neq 0$ when the induced electric force has a greater effect than ∇n_0 . In Figure 4, the particle moves upward away from the plane, and the general behavior of the stream function is similar to that for $\phi_r < 0$ and $\beta = -0.2$. However, Figure 5 shows that the particle moves downward to the plane. If the effect of the concentration gradient is greater than that of the electric field resulting from the discrepancy of ionic diffusion

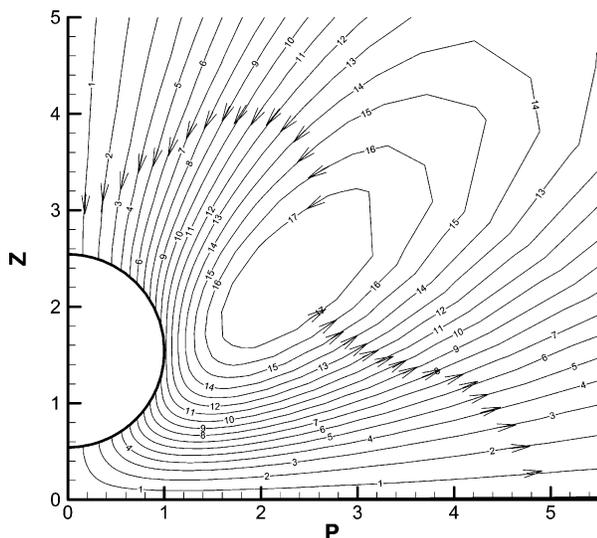


Figure 5. Contours of stream function ψ^* at $\beta = -0.2$, $\eta_0 = 1.0$, $\kappa a = 1.0$, $\phi_r = 2.0$, and $\alpha = 1$.

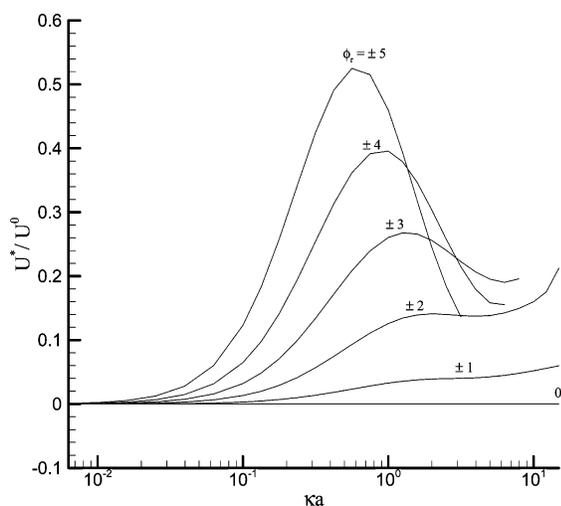


Figure 6. Variation of scaled diffusiophoretic velocity (U^*/U^0) as a function of κa at various values of ϕ_r when $\eta = 1.0$, $\beta = 0.0$, and $\alpha = 1$.

velocities, the direction of particle movement will be the same as that of the concentration gradient; otherwise, they will be opposite to each other. The flow field is much more complicated at distinct diffusion velocities for cations and anions than the corresponding identical situation.

Influence of Double Layer Thickness and Surface Potential. Generally speaking, thinner double layer (higher κa) or higher ϕ_r results in a greater velocity of the particle because ion concentration increases with the increase of κa , as revealed by eq 12. The electric double layer represents the range of ϕ_r which can affect the ion distribution. More counterions are attracted within the double layer as the electrostatic interaction between charged particle and counterions gets stronger when ϕ_r gets high. The driving force exerted upon the particle increases as a result. Nevertheless, the particle does not accelerate all the way with increasing ϕ_r in Figures 2 and 3. It actually reaches a local maximum at some ϕ_r first, and then decreases thereafter. In other words, when ϕ_r exceeds a certain threshold value, the velocity of the particle no longer increases monotonously with it. In order to explain what happens there, we use κa as abscissa in Figures 6 to 8 for convenience. In these figures, we see similar behaviors over a certain range of κa . This phenomenon was analyzed in details by Lee et al. in

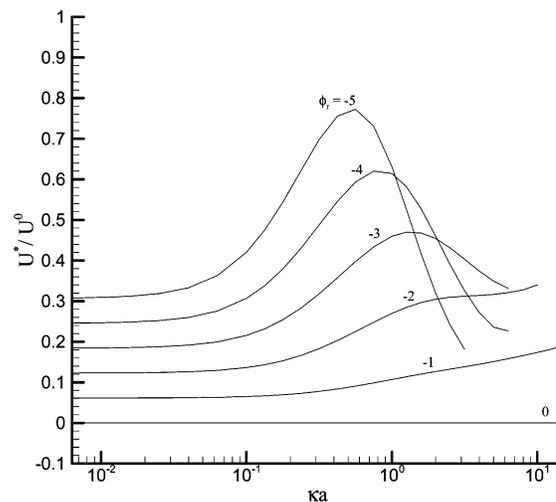


Figure 7. Variation of scaled diffusiophoretic velocity (U^*/U^0) as a function of κa for negatively charged particle when $\eta = 1.0$, $\beta = -0.2$, and $\alpha = 1$.

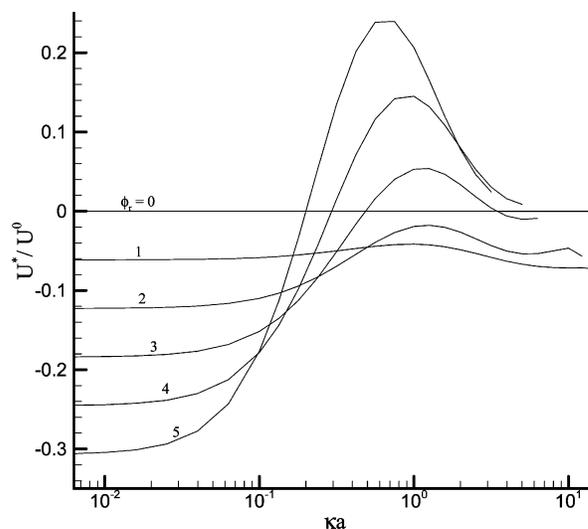


Figure 8. Variation of scaled diffusiophoretic velocity (U^*/U^0) as a function of κa for positively charged particle when $\eta = 1.0$, $\beta = -0.2$, and $\alpha = 1$.

studies of both electrophoresis³³ and diffusiophoresis,^{20,21} and they stem from the polarization effect of the electric double layer surrounding the charged particle. When a charged particle is driven by an applied concentration gradient of ions, the counterion distribution in the neighborhood of the charged particle instantly becomes nonconcentric to the spherical particle. This nonuniform distribution of counterions results in an induced electric field so that the electric potentials next to the particle surface are different in the front and the rear ends of the double layer. This distortion of electric double layer is normally referred to as the polarization effect. The polarization effect due to the induced electric field always opposes the normal diffusiophoretic motion. As the gradient of electric potential increases with thinner double layer (larger κa) or as surface potential on the particle gets higher (larger ϕ_r), both result in an increase of the driving force for particle motion will increase. The opposing electric force due to polarization, however, gets stronger at the same time. When the latter prevails in the net outcome, the scaled diffusiophoretic velocity (U^*/U^0) will decrease with increasing ϕ_r or κa over some range of κa , as shown in Figures 6 and 7. In their study of the diffusiophoresis of an isolated particle, Prieve and Roman¹⁷ claimed that it was still possible that the movement of the colloidal particle might change the

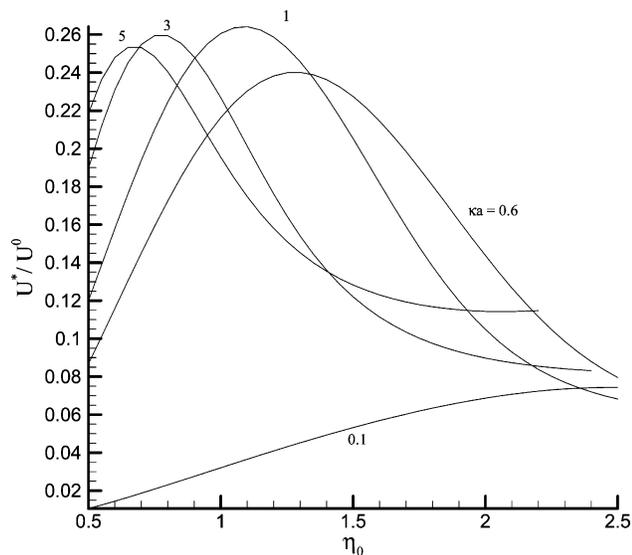


Figure 9. Variation of scaled diffusio-phoretic velocity (U^*/U^0) as a function of η_0 at various values of κa when $\phi_r = \pm 3.0$, $\beta = 0.0$, and $\alpha = 1$.

direction at high ϕ_r and medium κa , even when the diffusion speed for cations is equal to that for anions. Subsequently, Pawar et al.⁴⁰ showed that the reversal in direction of particle motion was due to the polarization effect. Lee and co-workers^{20,21} extended this observation to a system of concentrated dispersion. They found that the polarization effect is critically important when ϕ_r is sufficiently high and the double layer thickness is comparable to the radius of charged particle. We show here that exactly the same kind of behavior can be observed in the system under consideration. The polarization of double layer has the effect of reducing the driving force arising from the applied concentration gradient, and the higher the ϕ_r is, the more significant the polarization effect. Moreover, for a positively charged particle, the behavior is even more complicated as it is determined by two competing forces of concentration gradient and ionic diffusion,²¹ especially when ϕ_r is high, as seen in Figure 3. Generally speaking, the polarization effect has to be considered as ϕ_r and κa are sufficiently large. Thus, a small change in κa results in great variations in mass and electric potential flow. As a result, the direction of particle motion might alter more than once, as shown in Figure 8.

Influence of Planar Boundary. The effect of planar boundary, measured by $\eta_0 = \cosh^{-1}(h/a)$, on the scaled diffusio-phoretic velocity (U^*/U^0) is illustrated in Figures 9 to 11. According to the definition of η_0 , η_0 is a measure of the distance between the particle and the planar boundary. The smaller the η_0 is, the closer the two entities. It should be noted that van der Waals forces⁴¹ of attraction are beyond the scope of this work in order to focus on the specific mechanism of diffusio-phoresis resulted from the transport of ions within the double layer. Once again, it has to be reminded that the competition between chemi-phoresis and electrophoresis exists nonetheless when $\beta \neq 0$. By the same reasoning as adopted in analyzing results shown in Figures 2 and 3, the diffusio-phoretic velocities in Figure 10 are expected to be faster than those in Figure 9, which is supported by actual calculation results. Moreover, the particle is found to move in reversed direction if the particle is positively charged and the value of β is negative, as shown in Figure 11. However, Figures 9–11 reveal that for a fixed value of κa the diffusio-phoretic velocity of a particle does not increase monotonously with its distance from the plane, contrary to the situation in electrophoresis.^{32,33} In electrophoresis,^{32,33} it is

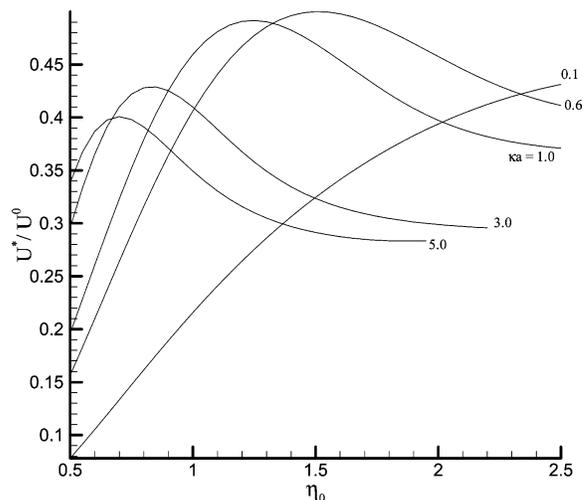


Figure 10. Variation of scaled diffusio-phoretic velocity (U^*/U^0) as a function of η_0 at various values of κa when $\phi_r = -3.0$, $\beta = -0.2$, and $\alpha = 1$.

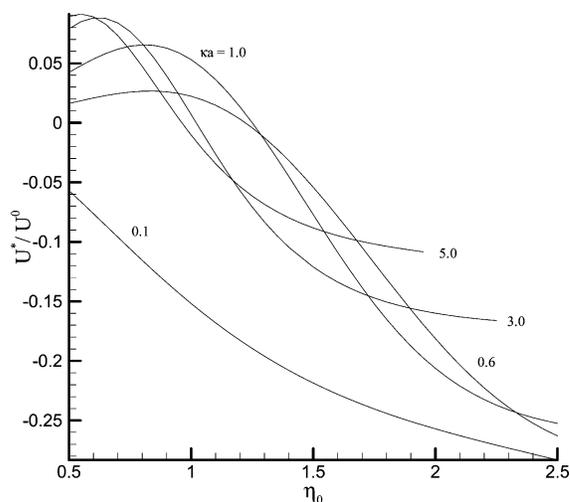


Figure 11. Variation of scaled diffusio-phoretic velocity (U^*/U^0) as a function of η_0 at various values of κa when $\phi_r = 3.0$, $\beta = -0.2$, and $\alpha = 1$.

anticipated that the closer the distance between the particle and the planar wall is, the more significant the hydrodynamic hindrance owing to the presence of the plane, hence the particle moves ever faster with the increase of η_0 . However, all of the scaled diffusio-phoretic velocities (U^*/U^0) shown here exhibit local maxima roughly a constant value of η_0 , when κa is either medium or large, and it approaches a constant value if η_0 is sufficiently high. Keh and Jang²⁹ were the first who noted this behavior in their study of diffusio-phoresis of a sphere normal to a plane. They found that the particle velocity increases monotonously with the increasing distance of the particle center from the wall in nonelectrolyte solution. For the case of diffusio-phoresis in electrolyte solution, however, they found both the magnitude and the direction of the particle velocity could vary as the particle approached the plane. Unfortunately, they were unable to discuss this observation further and find out the reason behind it, because of the limitation of thin double layer imposed by their approach.

In fact, this seemingly complicated behavior can be explained from the standpoint of a competition between the hydrodynamic resistance due to the planar boundary and the electric potential gradient due to the applied concentration gradient. As the gap between particle and planar boundary becomes narrow, the

hydrodynamic drag force stemming from planar boundary on the particle increase rapidly. Meanwhile, the double layer surrounding the particle might touch the plane as η_0 decreases. Hence, its distribution might be deformed because of the impervious solid plane. As mentioned before, the electric double layer represents the range of surface potential of the particle which can affect the ion distribution. Inside the double layer, counterions dominate. Thus, the deformation of double layer essentially puts more counterions at the front end of the particle, resulting in an induced local concentration gradient of counterions within the double layer. Following Dukhin's analysis,⁴ the externally imposed ion concentration gradient determines concentration profile of the region adjacent to the outer boundary of the double layer. In order to maintain the local electrical neutrality, the counterions within the double layer will redistribute in conjunction with the applied concentration gradient. Hence, the concentration distribution of counterions within the double layer must be parallel to the direction of the applied concentration gradient; that is, more counterions within the double layer accumulate at the front end of the particle as the gap thickness is narrower than the double layer. This will generate a diffusion flow of counterions moving toward the lower concentration region thus pushing the particle to move upward along the direction of applied concentration gradient. Moreover, the hydrodynamic boundary effect diminishes as the particle moves away from the plane. Hence, we can observe through Figures 9–11 that the diffusiophoretic velocity increases with the increase of η_0 at first. This effect of diffusion flow gets more significant for distinct ionic velocities ($\beta \neq 0$), which explains the discrepancy between velocities in Figure 9 and those in Figures 10 and 11.

As the particle is moving away from the plane, indicated by an increasing η_0 , the hydrodynamic drag force will gradually diminish; however, the effect of bulk concentration gradient on the counterions within the double layer will reduce as well! Taking into account these two opposing effects simultaneously, the particle thus moves with a velocity slower than expected from the sole consideration of hydrodynamic retarding effect. This is particularly noticeable at the very moment when the double layer is about to detach the plane: the effect of bulk concentration gradient within the double layer gradually disappears; hence, the counterion distribution within the double layer becomes more concentric to the particle, which results in a slower motion as η_0 increases. Note that this effect of the increase and decrease in particle velocity becomes more and more pronounced as κa increases. Examining the velocity behavior closely at each κa , we notice that the local maximum of the scaled velocity arises when the relative distance from particle surface to the plane is nearly the same as the double layer thickness. As shown in Figure 9, for example, the local maximum of the scaled velocity when $\kappa a = 3$ can be found at $\eta_0 \approx 0.795$, corresponding to the ratio of $a/(h - a)$, which represents the dimensionless gap; $a/(h - a)$ is at about 3.001, very similar to the value of κa . However, some deviations can also be found in Figure 10 and Figure 11 because there is an additional electrophoretic effect due to distinct diffusivities for cations and anions. The local maximum of the scaled velocity appears at a larger value of η_0 if the induced electric force due to $\beta \neq 0$ is in the same direction of the applied concentration gradient (which is, $\beta = -0.2$ and $\phi_r < 0$ in Figure 10). In contrast, a smaller value of η_0 is observed if the induced electric force acting on the particle surface is in the opposite direction of the applied concentration gradient. Because of the constraint of numerical convergence, the value of η_0 cannot be larger than

2.5 in the present calculations. However, it is anticipated that the diffusiophoretic velocity would tend to the results in the corresponding infinitely dilute solution¹⁷ as η_0 approaches infinity, judging from the current trend of (U^*/U^0) behavior.

Conclusion

Diffusiophoresis of a spherical particle normal to a solid plane in an electrolyte solution is analyzed here for arbitrary double layer thickness and surface potential. Previous restriction of very thin double layer is removed, and the general proper treatment of double layer polarization is implemented. It is found that, if the diffusion coefficients of cations and anions in the electrolyte solution are identical to each other ($\beta = 0$), the diffusiophoretic mobility exhibits both a local maximum and a local minimum with varying ϕ_r and κa , owing to the polarization effect of double layer. In comparison, the diffusiophoretic mobility oscillates asymmetrically with varying ϕ_r as the diffusion coefficients of cations and anions are distinct ($\beta \neq 0$). The movement of the particle is not always toward the higher bulk concentration of the electrolyte even when the sign of the zeta potential remains the same. Furthermore, the motion of the particle is greatly influenced by the hydrodynamic drag force and the applied concentration gradient if the particle is sufficiently close to the plane. In addition to the hydrodynamic retarding effect, the physical presence of the planar boundary also suppresses the counterion distribution adjacent to the particle. As the particle moves close to the planar boundary, the diffusiophoretic velocity of the particle is determined by the following factors: the charged condition on the particle surface, the bulk electrolyte concentration, the diffusion velocity of the solute, and the distance between the particle and the planar boundary (η_0). It is not always a monotonously increasing function with increasing η_0 . It may speed up at first and then slow down at some specific η_0 , resulting in a local maximum of velocity profile. In summary, the presence of a planar wall has a significant and complicated impact on the diffusiophoresis.

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