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Diffusiophoresis of Concentrated Suspensions of Spherical Particles with Distinct Ionic Diffusion Velocities

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The diffusiophoresis of a concentrated spherical dispersion of colloidal particles subject to a small electrolyte gradient is analyzed theoretically for an arbitrary zeta potential and double layer thickness. In particular, the influence of the difference in the diffusivities of cations and anions is discussed. A unit cell model is used to simulate a spherical dispersion, and a pseudospectral method is adopted to solve the equations governing the phenomenon under consideration. We show that, as in the case of an infinitely dilute dispersion, when the diffusivities of cations and anions are different, the diffusiophoretic mobility is no longer an even function of the zeta potential or double layer thickness. In contrast to the case of identical diffusivity of cations and anions, a local electric field is induced in the present case due to an unbalanced charge distribution between higher and lower concentration regions. Depending upon the direction of this induced electric field, the diffusiophoretic mobility can be larger or smaller than that for the case of identical diffusivity. The diffusiophoretic mobility is influenced mainly by the induced electric field arising from the difference in the ionic diffusivities, the concentration gradient, and the effect of double layer polarization.

Introduction

Concentration gradients of chemical species in an isothermal gas or liquid mixture are known to cause movement of colloidal particles,[1−2] and the resulting motion is commonly referred to as diffusiophoresis.[3] The underlying concept was first proposed by Deryagin et al.,[3−6] where the importance of this effect was demonstrated in the kinetics of film formation from lattices by ion deposition. In particular, the original primary theory was further extended to cases of general electrolyte solutions.[3] The growth rate of the latex film on the solid shape with diffusiophoresis would be comparable in magnitude to the conventional electrodeposition process, where hundreds of volts of electric power are required. Moreover, the Joule heating effect may be generated in the above-mentioned conventional process when an electric field is applied across conductive liquids. Such an effect is not welcomed in that the temperature will increase, which has a negative impact on electrophoretic motion.[7−8] The proposed new process with diffusiophoresis phenomena can avoid this undesirable heating effect.

A corresponding theoretical analysis was also carried out by Dukhin and Deryagin[3,6] and experimentally verified in both electrolyte and nonelectrolyte solutions as well.[9−11] It was shown by Deryagin and Dukhin[6] that diffusiophoresis is caused by the polarization of the double layer under the influence of a bulk concentration gradient. The relative motion between electrolyte solutes and charged particles is very complicated, especially in electrolyte solutions. Under the conditions of a thin double layer, symmetric binary electrolyte, constant applied concentration gradient, and isolated sphere in an unbounded solution, Dukhin and Deryagin[3] derived

$$\mathbf{U}^* = \frac{\epsilon\zeta}{\mu}\frac{k_BT}{ze}\frac{\nabla \mathbf{n}^\infty}{n_0}[\beta + \bar{\zeta}^{-1}\ln(\cosh\bar{\zeta})] \qquad (1)$$

where $\mathbf{U}^*$ is the diffusiophoretic velocity, ∇n^∞ is the applied concentration gradient, ze is the charge carried by a single ion, k_B is the Boltzmann constant, T is the temperature, ζ is the zeta potential, ϵ and μ are respectively the permittivity and the viscosity of the fluid, n_0 is the bulk electrolyte concentration measured with the absence of colloidal particles and a concentration gradient, and $\bar{\zeta} = ze\zeta/4k_BT$. $\beta = (D_1 - D_2)/(D_1 + D_2)$, D_1 and D_2 are respectively the diffusion coefficients of cations and anions, and β is a dimensionless parameter, which is an experimentally measurable property. For example, in an aqueous solution, β values are respectively 0, −0.2, and 0.64 for KCl, NaCl, and HCl.[12] A negative value of β implies that the diffusion velocity of anions is greater than that of cations. The appearance of β in eq 1 demonstrates clearly the involvement and quantitative contribution of this important parameter in determining the diffusiophoretic mobility, at least in that limiting case.

If the diffusion velocity of cations is different from that of anions, $\beta \neq 0$, the distribution of ionic species in the neighborhood of a particle becomes asymmetric yielding an induced electric field. This induced field then exerts an extra electric force on the particle, in addition to that caused solely by the concentration gradient, as in the case when $\beta = 0$. This can be deduced directly from eq 1 also, where a nonzero β alters the eventual diffusiophoretic velocity $\mathbf{U}^*$. Dukhin and co-workers[13−15] were the first group to notice this phenomenon. They observed that in a suspension of colloids dispersed in a NaCl aqueous solution, as the sign of the colloidal surface potential varied from negative to positive, the reversion of diffusiophoresis direction might take place accordingly more than four times. In summary, there are two contributions to the diffusiophoresis in general: one due to the imbalance of electrolyte charge which induces an electric field and thus is of the nature of electrophoresis ($\beta \neq 0$); the other due to the imbalance of the chemical potential, or more specifically here, the osmosis pressure, associated with the imbalance of electrolyte concentration ($\beta = 0$), sometimes referred to as the “chemiphoresis” by some groups. When $\beta = 0$, only the chemiphoresis mechanism exists, and when $\beta \neq 0$, both aspects are there.

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Based on Gouy–Chapman model,[1] Prieve and co-workers[16–20] further loosened the restriction of low zeta potential in their theoretical analyses and observed strong evidence supporting their proposed diffusiophoretic mechanism from experimental data. They found that colloidal particles might move toward the lower electrolyte concentration as $\beta \neq 0$ even though the zeta potential remained low. Dukhin[21] provided a thorough physical analysis for this later on. It was shown that the external concentration gradient could induce both a concentration and an electrical dipole moment, causing a nonequilibrium double layer near the particle surface. Pawar et al.[22] also used the thin double layer model to demonstrate the mechanism for the reversion of the particle motion. This phenomenon arises from the concentration polarization of the double layer surrounding a particle, which induces a local electric field opposing to the normal diffusiophoretic motion.[21] Aside from hard spherical particles, Baygents and Saville[23] also studied numerically the diffusiophoresis of a droplet and a small bubble suspended in an electrolyte solution. Misra et al.[24] explored the diffusiophoresis of a soft particle.

If the concentration of a colloidal dispersion is high, the existence of neighboring particles can no longer be ignored. In this case, the appropriate choice of conditions on the outer boundary is crucial. Therefore, theoretical studies on diffusiophoresis have been focused on systems with boundaries, physical[25] or virtual,[26,27] in recent years. However, these results were restricted to the low surface potential, taking no account of the electroosmotic flow of ions in the double layer. In our recent work on the case of $\beta = 0$,[28] we considered further the polarization effect at arbitrary zeta potential and double layer thickness on the diffusiophoretic mobility of colloidal particles. The osmotic flow of ions in the double layer is taken into account by the inclusion of convection term in the ion conservation equations. A particularly interesting result of our investigation was that the direction of particle motion could change at high zeta potentials and medium double layer thickness even when $\beta = 0$. We found there that the concentration polarization of the double layer here produced a coupled mass and charge flow near the surface of a particle, which made its motion much more complicated at high zeta potentials and medium double layer thickness.

In this study, our previous analysis for the case when $\beta = 0$[28] is extended to the general case when $\beta \neq 0$. The diffusiophoretic behavior of a spherical dispersion under the conditions of arbitrary surface potential and double layer thickness is analyzed thoroughly, with special focus on the electroosmotic flow induced by the distinct ionic diffusion velocities.[28] The influences of the key factors such as the thickness of double layer, relative diffusion velocities between cations and anions, zeta potential, and volume fraction of a suspensions on the diffusiophoretic mobility are examined as well.

Theory

Let us consider the diffusiophoresis of concentrated rigid spherical particles of radius a in a aqueous solution of z_1:z_2 where electrolytes z_1 and z_2 are respectively the valences of cations and anions. The electroneutrality in the bulk liquid phase requires that $n_{20} = n_{10}/\alpha$, n_{10} and n_{20} being respectively the bulk concentrations of cations and anions, and $\alpha = -z_2/z_1$. The dispersion is simulated by the unit cell model of Kuwabara.[29] Referring to Figure 1, the dispersion is modeled by a representative particle of radius a surrounded by a concentric spherical liquid shell of radius b. Let $\varphi = (a/b)^3$, which a measure of the volume fraction of the present dispersion.

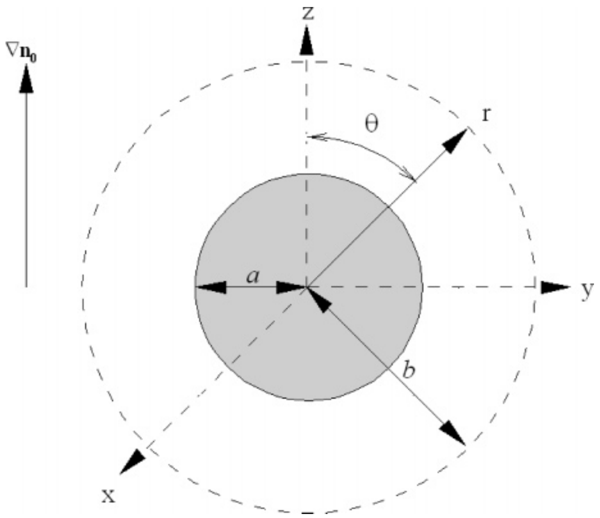


Figure 1. Schematic representation of the system under consideration where a is the radius of a particle and b is that of a liquid cell. The applied concentration gradient $\nabla \mathbf{n}_0$ is in the z-direction.

Suppose that a uniform concentration gradient $\nabla \mathbf{n}_0$ is applied to the system in the z-direction, and as a response, the particle moves in the z-direction with a constant velocity $\mathbf{U}$. The spherical coordinates (r,θ,ϕ) with the origin located at the center of the representative particle are adopted.

For the present problem, we have to solve simultaneously the governing equations for the electric, the flow, and the concentration fields. These equations can be summarized as below:

$$\nabla^2 \phi = -\frac{\rho}{\epsilon} = -\sum_{j=1}^{2} \frac{z_j e n_j}{\epsilon} \tag{2}$$

$$\nabla \cdot \mathbf{v} = 0 \tag{3}$$

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

$$\nabla \cdot \mathbf{f}_j = 0, \quad j = 1, 2 \tag{5}$$

$$\mathbf{f}_j = -D_j\left(\nabla n_j + \frac{n_j z_j e}{kT} \nabla \phi\right) + n_j \mathbf{v}, \quad j = 1, 2 \tag{6}$$

In these expressions, ϕ is the electrical potential, $\mathbf{v}$ is the liquid velocity, ρ and ϵ are respectively the space charge density, and the permittivity of the liquid phase, and e is the elementary charge. The terms n_j, $\mathbf{f}_j$, and D_j are respectively the number concentration, the concentration flux, and the diffusion coefficient of ionic species j. Also, p and μ are respectively the pressure and the viscosity of the liquid phase.

It is known that in a static environment n_j follows a Boltzmann distribution at equilibrium, if the electrolyte concentrations and particle's potentials are not too high, which is the case under study here. The two factors in our system are sometimes several orders of magnitude smaller than where significant deviations from the Boltzmann distribution were reported experimentally. Furthermore, to account for possible concentration polarization arising from the movement of particles in the present problem, we assume a modified Boltzmann distribution of the form:[30]

$$n_j = n_{j0} \exp\left(-\frac{z_j e}{k_B T}(\phi_e + \delta\phi + g_j)\right) \tag{7}$$

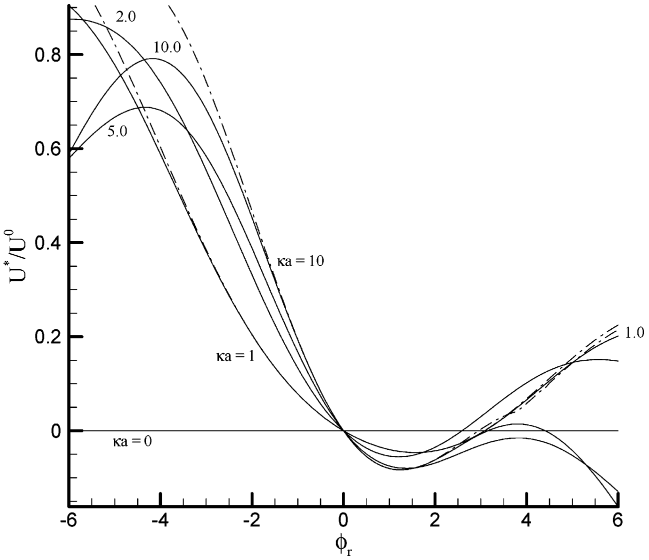


Figure 2. Variation of the scaled diffusiophoretic mobility (U^*/U^0) as a function of ϕ_r at various values of κa at $\varphi = 0.1$, $\beta = -0.2$, and $\alpha = 1$. The dashed curves are results for low surface potential.

That is, the electrical potential is decomposed into ϕ_e, $\delta\phi$, and g_j, representing respectively the equilibrium electric potential in the corresponding static problem, the induced electric potential arising from the movement of the liquid phase, and an equivalent perturbed potential arising from the convection of the electrolyte ions.

Note that diffusiophoresis can be characterized by an electrophoresis driven by the local gradient of electric potential coming from the bulk concentration gradient. This implies that the equations governing a diffusiophoresis problem can be deduced directly from those of the corresponding electrophoresis problem. It can be shown that the governing equations of the present problem, in dimensionless forms, are[28,30]

$$\nabla^2\phi_e^* = -\frac{(\kappa a)^2}{(1+\alpha)\phi_r}[\exp(-\phi_r\phi_e^*) - \exp(\alpha\phi_r\phi_e^*)] \quad (8)$$

$$\nabla^{*2}\delta\phi^* = -\frac{(\kappa a)^2}{(1+\alpha)\phi_r}\{\exp[-\phi_r(\phi_e^* + \delta\phi^* + g_1^*)] - \exp[\alpha\phi_r(\phi_e^* + \delta\phi^* + g_2^*)]\} + \frac{(\kappa a)^2}{(1+\alpha)\phi_r}[\exp(-\phi_r\phi_e^*) - \exp(\alpha\phi_r\phi_e^*)] \quad (9)$$

$$\nabla^{*2}g_j^* - \phi_r\nabla^*\phi_e^*\cdot\nabla^*g_j^* - \phi_r^{\ 2}Pe_j\mathbf{v}^*\cdot(\nabla^*\phi_e^* + \nabla^*\delta\phi^* + \nabla^*g_j^*) - \phi_r(\nabla^*\delta\phi^* + \nabla^*g_j^*)\cdot\nabla^*g_j^* = 0, \quad j = 1,2 \quad (10)$$

$$E^{*4}\psi^* = -\frac{(\kappa a)^2}{1+\alpha}\left\{\left[n_1^*\frac{\partial g_1^*}{\partial r^*} + n_2^*\frac{\partial g_2^*}{\partial r^*}(\alpha n_2^*)\right]\frac{\partial\phi^*}{\partial\theta} - \left[n_1^*\frac{\partial g_1^*}{\partial\theta^*} + n_2^*\frac{\partial g_2^*}{\partial\theta^*}(\alpha n_2^*)\right]\frac{\partial\phi^*}{\partial r^*}\right\}\sin\theta \quad (11)$$

where a symbol with an asterisk represents a dimensionless quantity. The term $\kappa = [\sum_{j=1}^{2} n_{j0}(ez_j)^2/\epsilon k_B T]^{1/2}$ is the reciprocal Debye length κ, $\phi_r = \zeta_a/(kT/z_1e)$ is the scaled zeta potential, with ζ_a as the zeta potential of particles. Also, $\phi_e^* = \phi_e/\zeta_a$, $\delta\phi^* = \delta\phi/\zeta_a$, $g_j^* = g_j/\zeta_a$, and $n_j^* = n_j/n_{10}$. Pe_j is the corresponding Peclect number of ion j, representing the effect of convection.

We assume that the surface potential of a particle remains constant and it is nonconductive. Also, the stern layer conductivity is neglected.[31] The net ionic flux across the virtual surface of a cell vanishes, so does the ionic concentration gradient. The particle surface is no slip. For convenience, we assume that the fluid is flowing toward a stationary particle with a scaled velocity U^*. On the basis of these assumptions, the boundary conditions associated with the present problem are as follows:

$$\phi_e^* = 1, \quad \text{at } r^* = 1 \quad (12)$$

$$\frac{\partial\phi_e^*}{\partial r^*} = 0, \quad \text{at } r^* = \frac{b}{a} \quad (13)$$

$$\frac{\partial\delta\phi^*}{\partial r^*} = 0, \quad \text{at } r^* = 1 \quad (14)$$

$$\delta\phi^* = -\frac{1}{\phi_r}\left(\frac{1}{Pe_1} - \frac{1}{\alpha^2 Pe_2}\right)\left(\frac{1}{Pe_1} + \frac{1}{\alpha Pe_2}\right)^{-1}(\nabla^* n_0^*), \quad \text{at } r^* = \frac{b}{a} \quad (15)$$

$$\frac{\partial g_1^*}{\partial r^*} = \frac{\partial g_2^*}{\partial r^*} = 0, \quad \text{at } r^* = 1 \quad (16)$$

$$\begin{cases} (\delta\phi^* + g_1^*) = -\dfrac{1}{\phi_r}(\nabla^* n_0^*) \\ (\delta\phi^* + g_2^*) = \dfrac{1}{\alpha\phi_r}(\nabla^* n_0^*) \end{cases}, \quad \text{at } r^* = \frac{b}{a} \quad (17)$$

$$\psi^* = 0, \quad \frac{\partial\psi^*}{\partial r^*} = 0, \quad \text{at } r^* = 1 \quad (18)$$

$$\psi^* = \frac{1}{2}r^{*2}U^*\sin^2\theta, \quad \text{at } r^* = \frac{b}{a} \quad (19)$$

$$E^2\psi^* = 0, \quad \text{at } r^* = \frac{b}{a} \quad (20)$$

where $r^* = r/a$, $(\nabla^* n_0^*) = \nabla\mathbf{n}_0/(n_{10}/a)$, and $E^{*4} = E^{*2}E^{*2}$ with

$$E^{*2} = \frac{\partial^2}{\partial r^{*2}} + \frac{\sin\theta}{r^{*2}}\frac{\partial}{\partial\theta}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\right) \quad (21)$$

The approach of Prieve and Roman[20] is adopted where it was assumed that the concentration of solute is only slightly nonuniform over the length scale a, that is, $a|\nabla\mathbf{n}_0| \ll n_0$. In this case, the present problem can be decomposed into two subproblems, where both are of linear nature.[20] In the first subproblem, a particle moves with a constant velocity in the absence of the applied concentration gradient, and in the second subproblem, it is fixed in the space when the concentration gradient is applied. If we let F_1 and F_2 be respectively the forces acting on the surface of a particles in these two subproblems, then $F_1 = f_1'(\nabla^* n_0^*)$ and $F_2 = f_2' U^*$, where f_1' and f_2' are proportional constants.[20] Consequently, the scaled diffusiophoretic mobility U_m^* can be expressed as

$$U_m^* = \frac{U^*}{E_z^*} = -\frac{f_1'}{f_2'} \quad (22)$$

Given the values of $\nabla^* n_0^*$ and U^*, F_1 and F_2 are calculated first through solving the entire set of electrokinetic equations; f_1'

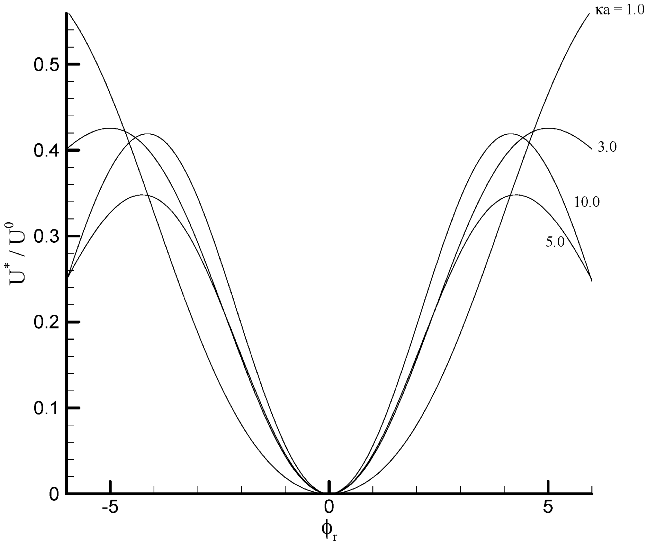


Figure 3. Variation of the scaled diffusiophoretic mobility (U^*/U^0) as a function of ϕ_r at various values of κa at $\varphi = 0.1$, $\beta = 0$, and $\alpha = 1$.

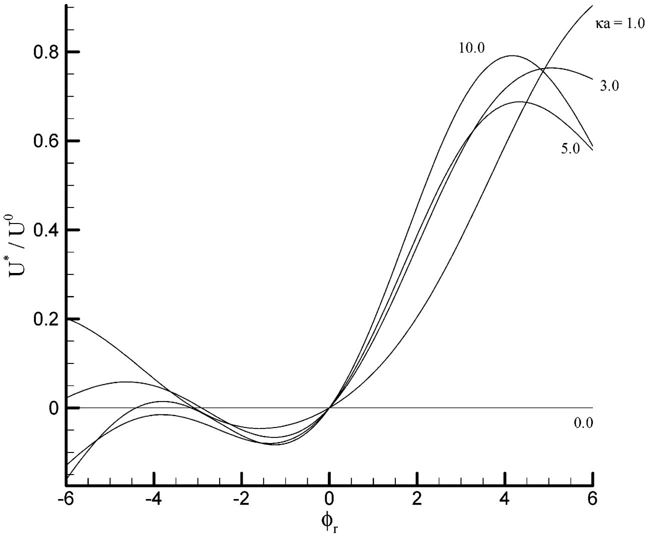


Figure 4. Variation of the scaled diffusiophoretic mobility (U^*/U^0) as a function of ϕ_r at various values of κa at $\varphi = 0.1$, $\beta = 0.2$, and $\alpha = 1$.

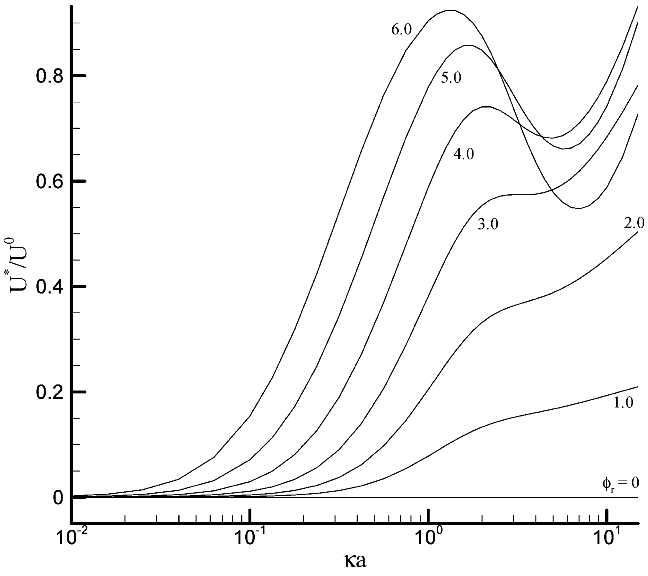


Figure 5. Variation of the scaled diffusiophoretic mobility (U^*/U^0) as a function of κa at various values of ϕ_r for $\phi_r \leq 0$, $\varphi = 0.1$, $\beta = -0.2$, and $\alpha = 1$.

and f_2' are then determined directly by their definitions, and U_m^* is calculated by eq 22.

Results and Discussion

Effect of Zeta Potential. The influence of the key parameters of the system under consideration on its diffusiophoretic mobility is examined through numerical simulation. For illustration, NaCl is chosen as the representative electrolyte, and we have $\alpha = 1$, $Pe_1 = 0.39$, $Pe_2 = 0.26$, and $\beta = -0.2$. Figure 2 shows the variation of the scaled diffusiophoretic mobility (U^*/U^0) as a function of scaled surface potential ϕ_r at various values of κa, where $U^0 = (\epsilon/\mu a)(kT/z_1e)^2$ is a characteristic diffusiophoretic mobility, which is proportioned to the velocity of a corresponding isolated sphere in an unbounded electrolyte solution with $\beta = 0$, under a unit concentration gradient.[3] For comparison, the results for the corresponding limiting case of low surface potential at $\kappa a = 1$(ref 26) and 10 (ref 27) are also presented. Figure 2 reveals that the result of low surface potential can be recovered as the limiting case of the present analysis by assuming a sufficiently low level of ϕ_r. Also, a level of $|\phi_r|$ lower than unity can be considered as sufficiently low. Note that if ϕ_r exceeds this level, the deviation of the result based on the low surface potential assumption from the exact value becomes significant. For $|\phi_r| \geq 5$, for instance, the deviation can be several fold.

Effect of Ionic Diffusion Coefficients. The influence of β on the diffusiophoretic behavior of a dispersion can be seen by comparing Figures 2 and 3, where $\beta = 0$ in the latter. Figure 3 indicates that if $\beta = 0$, (U^*/U^0) is an even function of ϕ_r. However, as shown in Figure 2, the symmetric nature of (U^*/U^0) with respect to ϕ_r no longer exists when $\beta \neq 0$. Similar behavior was also reported by Prieve[20] in an analysis of the behavior of an infinitely dilute dispersion, and it was concluded that the behavior of diffusiophoretic mobility is complicated when $\beta \neq 0$. Dukhin[21] referred to this conclusion and gave a very theoretical explanation for the complicated flow field. He proposed that the diffusiophoresis of a particle arises not only from chemiphoresis but also electrophoresis since the diffusion velocity of cations is different from that of anions ($Pe_1 \neq Pe_2$). Here, chemiphoresis refers to the fact that the motion of a charged particle is due to the nonuniform distribution of ions within the electric double layer, and electrophoresis refers to the induced electric field arising from the difference in the motion speed of cations and anions. This induced electric field is directed toward lower NaCl concentrations since the diffusivity of Cl^- is larger than that of Na^+. Malkin et al.[15] first predicted the inversion of diffusiophoresis direction, such as that seen in Figure 2 for $\phi_r > 0$, and later on, Dukhin[21] gave a detailed physical analysis of this mechanism. We find here that Dukhin's analysis for a dilute dispersion is also applicable to a concentrated dispersion, as will be elaborated below.

The chemiphoresis and the electrophoresis are reflected by the governing equations and the corresponding boundary conditions in two separate ways: the contribution from the ionic concentration gradient in eq 17, and the two Peclet numbers in eq 15 are not identical ($Pe_1 = 0.39$ and $Pe_2 = 0.26$). Thus, the eventual speed and direction of particle motion is determined by the balance of these two forces. Besides, according to eq 15, the direction of the induced electric force is determined by the specific charged conditions of a particle and the relative magnitudes of Pe_1 and Pe_2. For a negatively charged particle

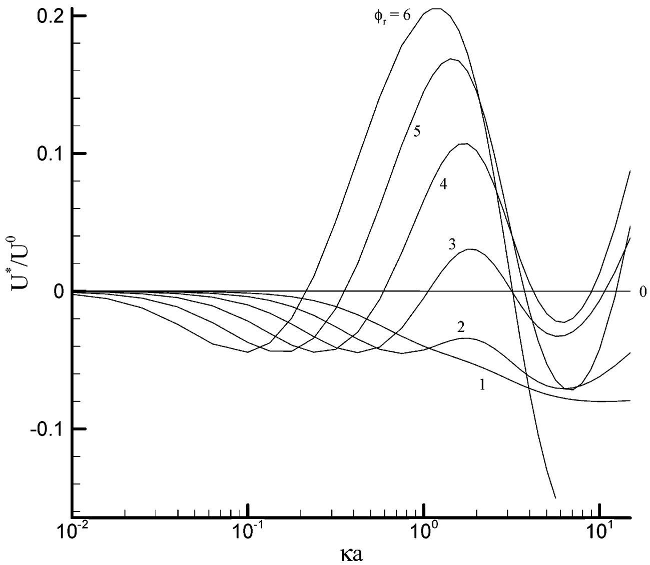
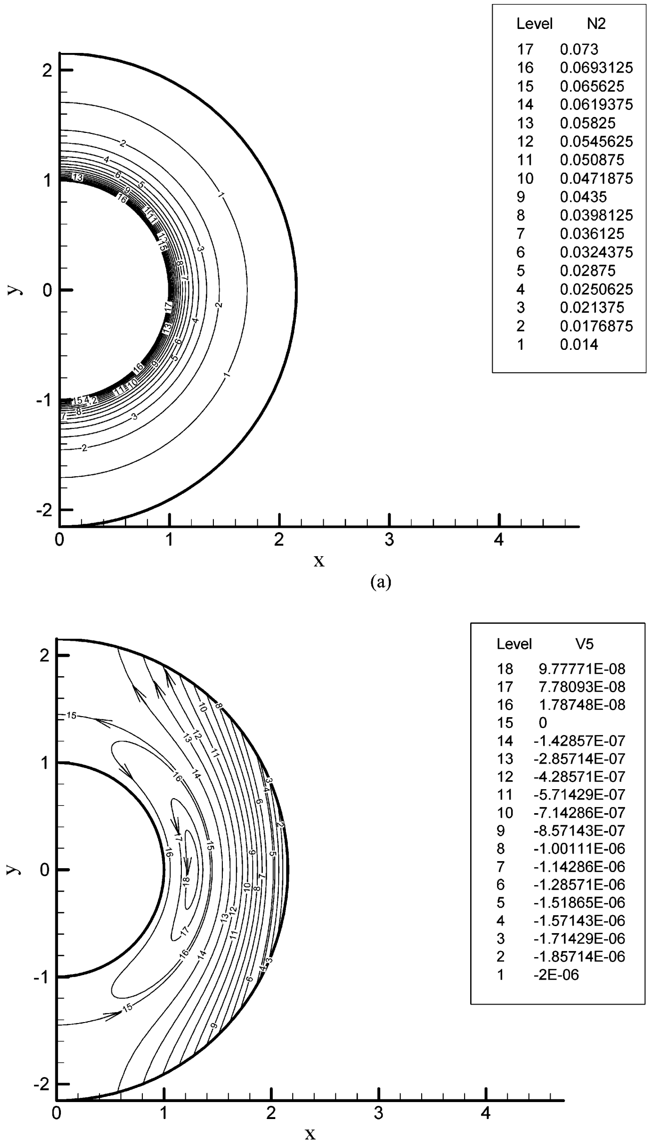


Figure 6. Variation of the scaled diffusiophoretic mobility (U^*/U^0) as a function of κa at various values of ϕ_r for $\phi_r \geq 0$, $\varphi = 0.1$, $\beta = -0.2$, and $\alpha = 1$.

($\phi_r < 0$), the direction of the induced electric force is the same as that of the major driving force provided by the applied concentration gradient. This is why the direction of particle motion shown in Figure 3 is always the same as that of the concentration gradient in Figure 2 when ϕ_r is negative. As illustrated in Figure 3, although originally (U^*/U^0) increases monotonically with the increase in ϕ_r, it does not increase all the way with increasing ϕ_r. It actually reaches a local maximum first and then decreases ever after. This is due to the polarization effect generated at a high enough ϕ_r or concentrated enough electrolytes.[28] For the same values of κa and ϕ_r, the magnitude of (U^*/U^0) in Figure 2 is larger than that in Figure 3. This is because when the diffusion velocities of cations and anions are different a particle can feel an additional electric force. For the case of positively charged particles, the concentration gradient competes against the induced electric field. As mentioned previously, the direction of the induced electric force is the same as the sign of the charge carried by a particle. Therefore, if $\phi_r > 0$ and sufficiently low, (U^*/U^0) is negative, as is seen in Figure 2. Moreover, as ϕ_r increases, the effect of concentration gradient becomes significant gradually as well, and eventually when it surpasses the effect of ionic diffusion, (U^*/U^0) will change from negative to positive. This is why the value of (U^*/U^0) on the left (right) half of Figure 2 is larger (smaller) than that of Figure 3. It is fully understandable from eq 1, which is based upon an unbounded solution, that (U^*/U^0) is not a simple even function of ϕ_r when $\beta \neq 0$. As illustrated in our recent result,[28] the illustration in infinite solution is also applicable to a concentrated suspension. In other words, whether (U^*/U^0) is symmetric about $\phi_r = 0$ is controlled by β.

We further examine the effect of β in more detail by letting $Pe_1 = 0.26$ and $Pe_2 = 0.39$, which gives $\beta = 0.2$ and a diffusion velocity of cations which is now greater than that of anions. In this case, instead of anions, cations are now cluster around the area of low concentration. Under this circumstance, the induced electric field is exactly opposite to that of the previous situation. Examining closely the overall behavior of (U^*/U^0) shown in Figure 4, one can see that the functional dependence of ϕ_r and κa are exactly opposite to that shown in Figure 2. We thus conclude that the sign and the magnitude of β are the key factors in the determination of the diffusiophoretic mobility.



(a)

(b)

Figure 7. Contours of counterionic concentration n_1^* (a) and stream function (b) at $\varphi = 0.1$, $\beta = -0.2$, $\phi_r = 2.0$, and $\alpha = 1$.

Effect of Double Layer Thickness. The variations of (U^*/U^0) as a function of κa, a measure for the thickness of double layer, at various values of ϕ_r are presented in Figures 5 and 6. This type of figure is capable of providing more insights about the overall behavior of a colloidal dispersion. For example, the polarization effect can easily be observed by the presence of the local maximum and/or minimum. Briefly speaking, a higher κa results in larger (U^*/U^0) because a higher κa means higher ionic concentrations. In other words, as κa increases, the amount of electrolytes increases accordingly in the vicinity of the particle surface, and hence the electric force exerted upon it increases accordingly. As discussed previously for the case when $\beta = 0$,[28] the local maximum and minimum shown in Figure 5 over some range of κa and ϕ_r arise from the polarization effect of the double layer surrounding a particle, which induces a microscopic electric field opposing to the normal diffusiophoretic motion. Moreover, for a positively charged particle, its behavior is much more complicated as it is determined by the competing concentration gradient and ionic diffusion under this circumstance,[21] especially when ϕ_r is high, as is seen in Figure 5. Besides, the polarization effect has to be considered as well when ϕ_r and κa are sufficiently large. Thus, a small

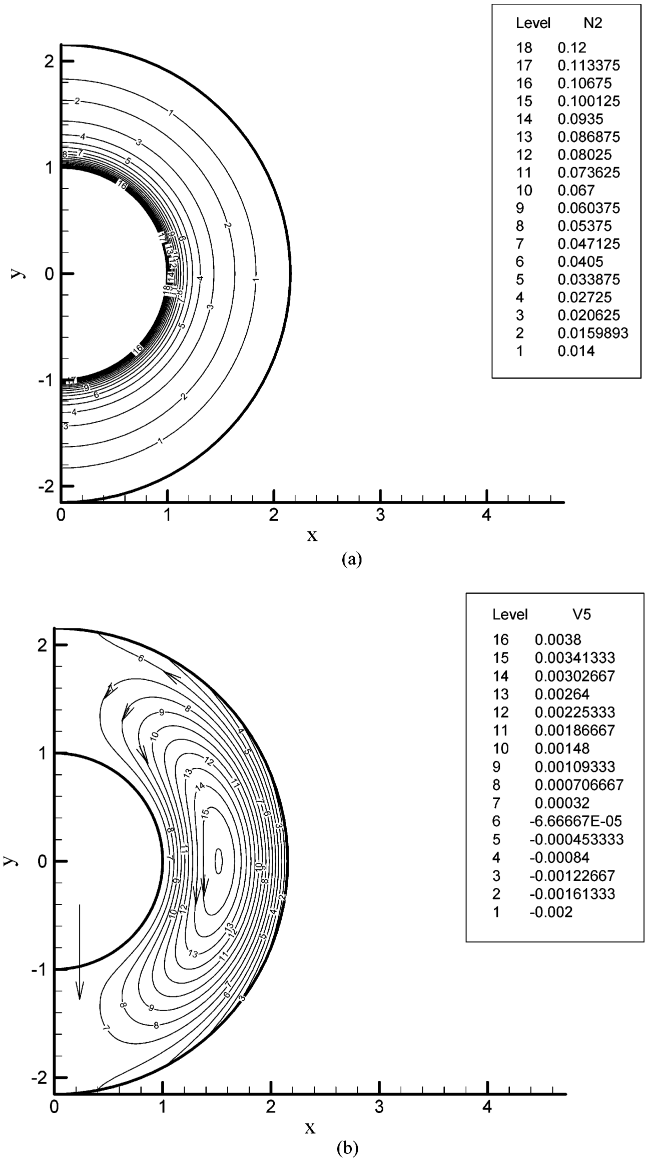


Figure 8. Contours of counterionic concentration n_2^* (a) and stream function (b) at $\varphi = 0.1$, $\beta = -0.2$, $\phi_r = 2.5$, and $\alpha = 1$.

change in κa results in great variations in mass and electric potential flow. As a result, the direction of particle motion is altered more than once, as shown in Figure 6.

Streamline Plots. To shed more light on the shadow, we further examine both counterions' distributions and the corresponding flow fields at various surface potential ϕ_r values, with κa fixed at 2.0; the simulated results are summarized in Figures 7 and 8. First, we observe that the distribution of counterions forms concentric spherical shells around a particle. With the increase of scaled surface potential ϕ_r, more counterions are attracted to the neighborhood of the particle surface. Checking further the concentration of counterions, we can determine whether a particle is negatively or positively charged. The concentration of anions decreases with the distance along the direction of concentration gradient, but that of cations increases. As explained earlier, this is because the diffusion velocity of anions is faster than that of cations, since $\beta < 0$. Due to the nonuniformity of the original overall bulk concentration, ions have a tendency to diffuse from high to low concentration areas, and since anions move faster than cations do, more anions would cluster in the lower concentration area, whereas more cations would stay in the high concentration areas.

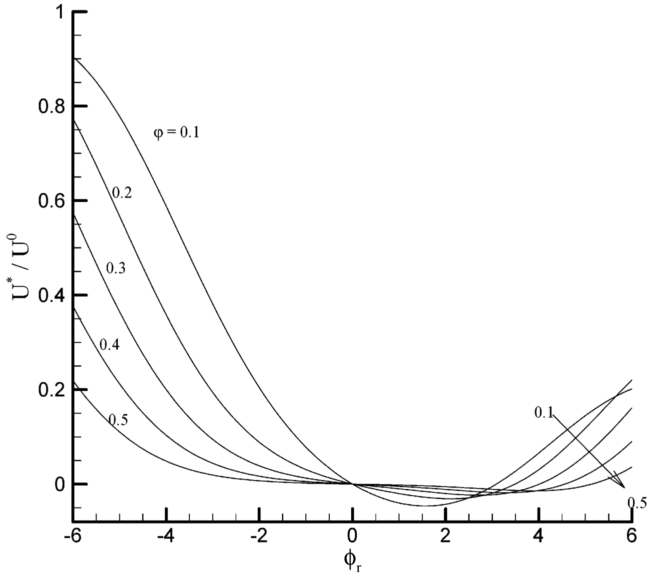


Figure 9. Variation of the scaled diffusiophoretic mobility (U^*/U^0) as a function of ϕ_r at various values of φ for $\kappa a = 1.0$, $\beta = -0.2$, and $\alpha = 1$.

This induces a nonequivalent charge distribution and results in an additional electric force. If a particle is positively charged, this electric force is directed toward the area of lower ionic concentration and opposite to the direction of concentration gradient. The ultimate direction of diffusiophoresis is determined by net result of these two driving forces. Figure 7b shows that for a positively charged particle, a separate counterclockwise vortex flow arises around the particle. As mentioned before, the diffusion flows of cations and anions lead to an accumulation of charges of opposite sign in different areas. The constraint of absence of net electric current requires generation of an electric field which causes a charge flow in a direction to compensate the charge difference between two sides. The direction of this ionic charge flow is determined by the surface charge of a particle, exactly as in electroosmotic flow. Observing this electroosmosis flow closely, we find that this counterclockwise vortex flow appears in the vicinity of the particle surface, with an opposite flow direction to retard the motion of the particle otherwise. In Figure 8b, the particle moves downward to the lower concentration side, but the electroosmotic vortex flow is rotating along the opposite direction. The competition between particle motion otherwise and this electroosmotic flow becomes more and more obvious as ϕ_r increases. If the effect of the concentration gradient is greater than that of the electroosmotic flow resulting from the discrepancy of ionic diffusion velocities, the direction of particle movement will be the same as that of the concentration gradient; otherwise, they will be opposite to each other. As the surface potential or electrolyte concentration becomes higher, that is, larger ϕ_r or κa values are exhibited, the competition of these two effects will continuously reconcile with each other and reach a new balance. The inside counterclockwise vortex flow due to electroosmosis grows so strong that it eventually "swallows" the original outside flow due to the concentration gradient. That is why it is possible that the number of direction changes in diffusiophoresis can be more than one when $\beta \neq 0$. In contrast, if a particle is negatively charged or $\beta = 0$, this phenomenon will not exist since the net diffusion flow of cations and anions vanishes.

Effect of Volume Fraction. Finally, we examine the influence of the particle concentration, measured by the volume fraction $\varphi = (a/b)^3$ of the colloidal particle in the electrolyte solution. The results are shown in Figure 9. Double layer overlapping is allowed in the current analysis. It is found that the diffusiophoretic mobility decreases with increasing volume fraction. This is mainly due to the hindrance effect of neighboring particles: the higher the concentration of colloidal particles, the more significant the overlapping of the neighboring double layers, leading to a greater hydrodynamic resistance for fluid flow in diffusiophoresis.

In summary, the diffusiophoresis of a concentrated colloidal dispersion is analyzed theoretically for the case when both the zeta potential and the thickness of a double layer can assume an arbitrary value, focused on the influence of distinct ionic diffusion velocities, measured by $\beta = (D_1 - D_2)/(D_1 + D_2)$, where D_1 and D_2 are respectively the diffusion coefficients of cations and anions. In contrast to the case when $\beta = 0$, the diffusiophoretic mobility exhibits specific oscillatory motion, and it is asymmetric with respect to the zeta potential when $\beta \neq 0$. The movement of a particle is not always toward the higher bulk concentration of the electrolyte even when the sign of the zeta potential remains the same. The sign and the magnitude of β are the key factors in determining the behavior of the diffusiophoretic mobility. Furthermore, we find that the influence of steric hindrance on the fluid flow must be taken into account as the colloidal dispersions become more and more concentrated.

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