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DIFFUSIOPHORESIS: MIGRATION OF COLLOIDAL PARTICLES IN GRADIENTS OF SOLUTE CONCENTRATION

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ABSTRACT

When a rigid colloidal particle is placed in a solution which is not uniform in the concentration of some solute that interacts with the particle, the particle will be propelled in the direction of higher or lower concentration of the solute. The resulting locomotion is called diffusiophoresis. Experimental observations and theoretical predictions of the migration velocity of hydrosols are reviewed. Present commercial applications include the formation of rubber gloves and the deposition of paint films onto a steel surface. New applications to the analysis of colloidal mixtures and solid-liquid separation are suggested.

INTRODUCTION

Driving forces for transport of colloidal particles generally include concentration gradients of the particles themselves (diffusion), electrical fields (electrophoresis), gravitational or centripetal fields (sedimentation) and pressure gradients (convection). Particle movement by a thermal gradient (Soret effect or "thermophoresis") is sometimes utilized in special applications. Another driving force for transport of colloids is a concentration gradient of a molecular solute.

"Diffusiophoresis" is the term broadly applied by B.V. Derjaugin[1,2] to the movement of a colloidal particle in response to a gradient of a molecular solute. Although he apparently

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intended this term to describe both fluid drops and rigid particles, we suggest it be used only for the motion of rigid particles; the motion of fluid drops should be considered a "Marangoni effect," that is, movement generated by a surface tension gradient. The reason for this distinction is based on the difference of the role of interfacial structure in the transport processes within the surrounding fluid. With the diffusiophoresis of rigid particles, it is essential that the interaction between solute and particle surface be diffuse (the particle velocity is proportional to the thickness of this diffuse interfacial layer). On the other hand, the velocity of fluid drops is independent of interfacial structure and is proportional to the drop radius instead of the interfacial thickness. Because we are concerned with particles and drops of order 1μm, which is very large compared to the thickness of the interfacial region, this difference means diffusiophoretic velocities are several orders of magnitude smaller than typical velocities of drops. The concept of a diffuse interfacial region, where solute and particle interact, is made more quantitative in the text where a numerical criterion to judge particle rigidity is developed.

Although diffusiophoresis of aerosols has been extensively studied,[3-6] there has been less attention given to diffusiophoresis of hydrosols. Perhaps this lack of attention has to do with the fact that the steep solute concentration gradients required usually occur only in the diffusion boundary layer, where many phenomena occur simultaneously. It is quite possible that diffusiophoresis has, in fact, had a significant but unrecognized effect on particle transport rates in boundary layers during coating processes and in porous membranes. There is no question that particle movement induced by a solute gradient is important in microbiology, where the term "chemotaxis" denotes the locomotion of living cells by gradients of chemical agents.[7]

Our purpose in this review is to explain the mechanism of diffusiophoresis and to discuss its importance as a transport process for colloids. For example, Smith & Prieve[8] showed that diffusiophoresis is the mechanism of a new commercial process for applying the first layer of paint on automobile frames and other metal surfaces. Acid and hydrogen peroxide, which are added to the dilute water-based paint, cause the iron in carbon steel to oxidize and dissolve at a rate limited by diffusion of reactants through the boundary layer next to the metal surface. The gradient in electrolyte concentration induces an electric field in the boundary layer which attracts negatively charged latex particles toward the metal surface. In this process, the induced gradient of electrical potential serves as the main driving force for diffusiophoresis of the latex particles. More generally, gradients in the electrochemical potential or chemical potential of the particle may serve as the driving force.

Although the model for diffusiophoresis which we discuss in subsequent sections utilizes surface science, mass transfer and fluid mechanics, an appreciation for the phenomenon can be gained from principles of thermodynamics. The energetics of the system are determined at the particle/solution interface which has associated with it an excess surface free energy per area (σ), sometimes called the "interfacial tension." One may consider σ of a fluid/fluid interface to be either a force per length or a free energy per area, but only the latter is reasonable for a solid/fluid interface. Suppose one spherical particle of radius $\underline{a}$ is transferred at constant temperature from a solution having solute concentration $C_{\infty 1}$ to another solution of concentration $C_{\infty 2}$. If the solute is "surface active" it adsorbs on the particle and lowers the interfacial tension from σ_1 to σ_2. The change in free energy is

$$\Delta G = 4\pi a^2(\sigma_2 - \sigma_1) \tag{1}$$

If $C_{\infty 2} > C_{\infty 1}$ then $\sigma_2 < \sigma_1$ and $\Delta G < 0$; thus, the particle would tend to move spontaneously.

The above conceptual experiment is now altered by imagining the particle to be in a solution in which C_∞ is a function of position. The gradient of free energy for one particle is

$$\nabla G = 4\pi a^2 \nabla\sigma = 4\pi a^2 \left(\frac{\partial\sigma}{\partial C_\infty}\right)_T \nabla C_\infty \tag{2}$$

Changes in surface free energy with changes in solute concentration under equilibrium conditions are related to the extent of solute adsorption through Gibbs equation,[9] which for dilute (thermodynamically ideal) solutions is

$$\left(\frac{\partial\sigma}{\partial C_\infty}\right)_T = \frac{kT\,\Gamma}{C_\infty} = -kT\,K \tag{3}$$

where Γ is the Gibbs "surface excess concentration" of solute (solute adsorbed to the surface per area), and $K \equiv \Gamma/C_\infty$ is called the "adsorption length,"[10] which is a measure of how strongly the solute is adsorbed as $C_\infty \to 0$. The above two equations indicate that, when the solute adsorbs on the particle, the particle can lower its free energy by moving toward regions of higher concentration. Thus from thermodynamics alone, one can prove that a particle will spontaneously migrate toward higher solute concentration.[11]

The limitation of models based on equilibrium thermodynamics is, of course, that they fail to predict how fast the particle moves. Attempts to estimate particle velocity on phenomenological grounds can lead to great error, as shown below. Suppose we make the reasonable postulate that velocity is proportional to the gradient of free energy:

$$\underline{U} = -\frac{1}{f}\nabla G \tag{4}$$

where f is some friction coefficient. To proceed further, one must guess what f is; one plausible choice is Stokes law: $f=6\pi\eta a$, where η is the solution viscosity. When combined with equations (2)-(4) this choice gives

$$\underline{U} = \frac{2}{3}\,\frac{aK\,kT}{\eta}\,\nabla C_\infty \tag{5}$$

which, as shown in subsequent sections, is wrong. It turns out that Stokes law is not appropriate here. Because diffusiophoresis results from a coupling between interfacial forces and fluid mechanics, one must address the transport phenomena occurring within the interfacial region at the particle/solution boundary in order to relate correctly the particle velocity to the physicochemical properties of the solution. Although the interfacial region may only be of order 10Å thick, we will apply the continuum equations of mass and momentum transport in this region, as found in the theoretical models for electrokinetic phenomena.[2,12]

As motivation for an analysis of transport in the interfacial region, consider the interfacial-tension-driven movement of fluid drops. When a drop is placed in a gradient of surface-active solute, the high concentration (forward) pole of the drop experiences a lower surface tension than the rear pole. Expansion of regions with a low interfacial tension and contraction of regions with a high interfacial tension propels the drop toward higher solute concentration. When the solute cannot enter the drop, the drop velocity is

$$\underline{U}_M = \frac{aK\,kT}{3\eta_i+2\eta}\,\nabla C_\infty \tag{6}$$

where η_i is the viscosity of the fluid inside the drop and K is defined by (3). This expression was derived by Young et al.[13] for a thermal gradient but applies equally well to a solute gradient, assuming the Peclet number is much less than one.[14] The subscript M is used to emphasize that this motion is a Marangoni effect, in which all interfacial phenomena can be lumped into an interfacial tension acting at the plane of the drop surface; that is, the structure of the interfacial region need not be known. Note that if the drop is made rigid ($\eta_i \to \infty$) then $\underline{U}_M \to \underline{0}$, and hence the usual analysis for Marangoni motion does not predict diffusiophoresis.

Credit must go to Derjaguin and his coworkers[1,2,15-17] for first predicting diffusiophoresis of rigid particles and elucidating the basic physical principle behind it. When the adsorbed layer of solute is diffuse, a tangential gradient in hydrostatic pressure arises inside it which causes fluid elements to accelerate until the net force is balanced by viscous stress. From this force balance Derjaguin et al.[15] obtained the following expression for the relative velocity between a planar solid surface ($y=0$) and the distant fluid ($y \to \infty$) in which there exists a gradient $\frac{dC_\infty}{dx}$ in the concentration of an uncharged solute:

$$U_{rel} = V(\infty) - V(0) = -\frac{kT}{\eta}\left(\frac{dC_\infty}{dx}\right)\int_0^\infty y\left[\exp\left(\frac{-E(y)}{kT}\right) - 1\right] dy \qquad (7)$$

$E(y)$ is the energy of one solute molecule at distance y from the solid surface. "Adsorption" means $E < 0$, where by definition $E \to 0$ as $y \to \infty$. Equation (7) indicates that if the solute adsorbs to the solid, then the fluid flows toward lower solute concentration, assuming the solid surface is the pore wall of a membrane which is mechanically held fixed. If such a membrane, with sufficiently large pores, separates two reservoirs of solute having different concentrations but equal pressure, (7) predicts a spontaneous flow from high to low concentration;* such an "osmotic" flow has been observed.[17]

Derjaguin did not explicitly analyze the movement of particles in Ref. 15. Instead he considered (7) to be a slip velocity between the fluid and a solid whose mean radius of curvature is sufficiently large that its surface appears flat at the length scale (L) of the interfacial region. By changing the frame of reference to allow the solid to move and the fluid be stationary

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*Osmosis is usually thought of as a solvent flow from lower to higher concentration through a "semipermeable" membrane which totally excludes solute. In the case discussed here, the porous membrane actually adsorbs solute, rather than rejects it, and hence flow is in the opposite direction.

at $y \to \infty$, he inferred the particle velocity to be $-U_{rel}$; that is, the particle moves toward higher solute concentration as expected from thermodynamic arguments. A more rigorous analysis[18] of particle motion shows Eq. (7) to be correct only if the particle radius is much greater than both L and the adsorption length K.

Derjaguin also considered solutes which ionize. With electrolytes there are two mechanisms for motion.[19] First, adsorption of ions into the diffuse part of the double layer produces a contribution to the particle velocity which is analogous to that for nonelectrolytes, except that there are now two solute species — the counterion, which is attracted to the charged particle, and the co-ion which is repelled. Deraguin *et al.*[1] calculated their effects separately using Eq. (7) and then added them. For convenience, we denote the net contribution from ion adsorption as "chemiphoresis." The second mechanism (which we call "electrophoresis") results from the electric field induced by the solute gradient when the cation and anion have different mobilities.[20] This induced electric field exerts a force on the charged particle just as an applied electric field does. Although chemiphoresis always pulls the particle toward higher electrolyte concentration, electrophoresis could cause motion in either direction depending on the sign of the particle's charge. Thus, diffusiophoresis caused by electrolytes can result in motion either up or down the solute gradient, whereas with nonelectrolytes the motion is always[*] up the gradient.

In this paper we discuss diffusiophoresis in terms of the physics and mathematics needed to understand it, experiments aimed at measuring it, and its importance to particle technology. We begin with a discussion of the role of interfacial phenomena in the coupling of fluid mechanics to mass transfer. This coupling, which occurs in an interfacial region whose thickness

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[*] In principle, a repulsive interaction between the solute and the particle could cause motion in the opposite direction, but the integral in (7) is severely limited in magnitude when $E(y) > 0$.

is tens of Ångstroms, determines the macroscopic rate processes. It is essential to appreciate what happens within this interfacial layer in order to understand why rigid particles move in concentration gradients. We then consider particle movement when the interfacial region is thin relative to the particle size. In this limit the relationship between particle velocity and solute gradient is independent of particle shape, as for electrophoresis. The movement of fluid drops is re-examined, this time with allowance for an interface of finite thickness, to demonstrate how the Marangoni result (Eq. (6)) can be reconciled with the diffusiophoretic result as the internal viscosity of the drop becomes large. We then move to the analysis of particle motion when the dimension of the interfacial layer is not infinitesimal to develop criteria for validity of the thin-layer results. We end with a discussion of experimental attempts to measure diffusiophoretic velocities, and of the importance of diffusiophoresis as both a transport mechanism and a basis from which analytical methods could be developed for inferring interfacial properties of colloids.

THE INTERFACIAL REGION

The Equilibrium State:

The adsorption of an uncharged molecular solute from a fluid phase onto a solid surface is quantitatively described by the Gibbs "surface excess" concentration Γ (moles per area). As Figure 1 indicates, adsorbed solute does not necessarily stick as one layer to a surface but, in general, could be distributed non-uniformly over a layer of thickness L which represents the interfacial region.

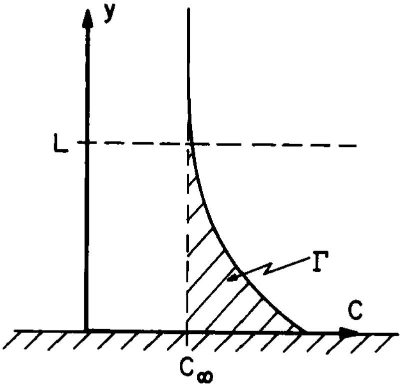

FIGURE 1
Profile of solute concentration inside interfacial region.

The surface excess concentration is defined as[9]

$$\Gamma = \int_0^\infty [C(y) - C_\infty]\, dy \qquad (8)$$

where C_∞ is the solute concentration in the bulk fluid phase. Also, L represents the distance from the surface over which C varies appreciably from C_∞; it is expected to be of order 10Å.

A second length scale is the adsorption length:

$$K \equiv \frac{1}{C_\infty}\int_0^\infty [C(y) - C_\infty]\, dy \quad , \qquad (9)$$

which can be interpreted as the thickness of a bulk solution layer that has to be stripped of solute to account for the excess Γ. Several points should be made about K. First, it is a mass-equivalent length and not a physical length. Second, the magnitude of K is a measure of the strength of adsorption: K >> L means the solute strongly adsorbs. It is not uncommon for K to be as large as 1μm.[10] Third, K (and hence Γ) could be negative if solute is repelled from the surface, as is the case with simple electrolytes at the air/water interface. We shall demonstrate that K as well as L are essential parameters in the physics of diffusiophoresis.

A positive value of Γ implies that the pressure is greater inside the interfacial region than in the bulk fluid. At infinite dilution, the Gibbs equation is given by (3). Theories of the mechanics of the interface[21,22] can be used to relate the decrease in interfacial free energy, caused by a change in solute concentration, to the integral average of the excess interfacial stress.

$$\sigma_o - \sigma = \int_0^\infty (p - p_\infty)\, dy \qquad (10)$$

where σ_o is the interfacial free energy when $C_\infty = 0$ and $p - p_\infty$ is the excess pressure due to the solute adsorption. Solute-solute interactions are neglected in (10); so the solute effect on the interfacial stress is isotropic. At higher solute concentrations, where solute-solute interactions are significant, this isotropy is lost.[23]

Assuming K is independent of C_∞, (3) and (10) are combined to give

$$\int_0^\infty (p-p_\infty)\, dy = C_\infty K\, kT = \Gamma kT \quad , \tag{11}$$

which clearly demonstrates that $p > p_\infty$ within the interfacial region if solute adsorbs to the surface. In addition to its mass-equivalent definition, K in (11) represents the distance over which the osmotic pressure $C_\infty kT$ acts on the fluid.

Of central importance is the distributed nature, or diffuseness, of the solute adsorption. A potential energy E(y) is defined in terms of the solute distribution using Boltzmann's equation:

$$C(y) = C_\infty \exp[-E(y)/kT] \tag{12}$$

where it can be shown[24] that $-E'(y)$ is a force acting on a solute molecule when it is at distance y from the surface. This energy represents the sum of solid-fluid-solute interactions relative to fluid-solute interactions in bulk fluid; thus, $E \to 0$ as $y \to \infty$. At low concentrations this force is transmitted to the solvent to establish a pressure gradient across the interfacial region:

$$\frac{dp}{dy} + C\,\frac{dE}{dy} = 0 \quad , \tag{13}$$

which when integrated with the help of (12) gives

$$p - p_\infty = C_\infty\, kT\, [\exp(-E/kT) - 1] \quad . \tag{14}$$

This expression is consistent with (9) and (11).

Flow Caused by Non-electrolyte Gradients

In the preceding section C_∞ was assumed uniform. Now consider a gradual variation parallel to the surface such that locally $C_\infty(x) = C_\infty(x_0) + (x-x_0)C'_\infty(x)$. If the distance over which C_∞ changes appreciably, C_∞/C'_∞, is large compared to L, one can assume that Eqs. (12)-(14) are valid locally. Although the pressure outside the interfacial layer (p_∞) is constant, there exists a tangential pressure gradient within the interfacial region because of the variation of C_∞, as seen from (14). As a result of this pressure gradient, the fluid elements accelerate until the viscous stress balances the pressure gradient:

$$\eta \frac{\partial^2 v_x}{\partial y^2} - \frac{\partial p}{\partial x} = 0 \qquad (15)$$

Boundary conditions are

$y = 0$: $v_x = 0$ (no slip at solid surface)

$y \rightarrow \infty$: $\frac{\partial v_x}{\partial y} \rightarrow 0$ (no pressure gradients in bulk fluid)

Substituting (14) into (15) and integrating twice gives

$$v_x = -\frac{kT}{\eta}\left(\frac{dC_\infty}{dx}\right)\int_0^y dy' \int_{y'}^{\infty} [\exp(-E(y^*)/kT) - 1]\, dy^* \qquad (16)$$

which predicts the profile qualitatively shown in Figure 2. Note that outside the interfacial region (i.e., $y \gtrsim L$), v_x takes on its asymptotic value as $y \rightarrow \infty$. Compared to the much larger radius of curvature of the surface, the thickness of the interfacial region over which v_x varies continuously from zero to its upper limit is so small that the value of v_x obtained by replacing y in (16) by ∞ can be treated as a "slip velocity" at the macroscopic scale. After

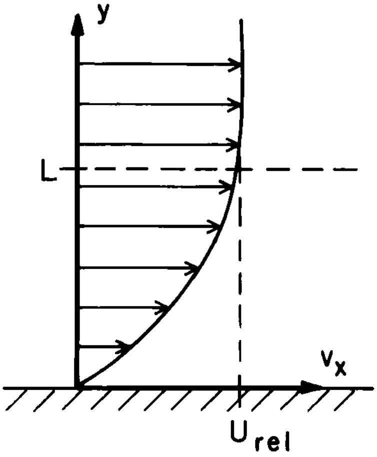

FIGURE 2
Velocity profile inside interfacial region.

integration by parts, this slip velocity is given by (7).

The form of (7) is not useful because there are no direct methods of measuring E(y). However, the integral is related to two length scales which characterize E(y):

$$U_{rel} = - \frac{L^*K\ kT}{\eta} \frac{dC_\infty}{dx} \tag{17}$$

where K is given by (9), or

$$K = \int_0^\infty [\exp(-E/kT) - 1]\ dy \tag{18a}$$

and

$$L^* = \frac{\int_0^\infty y[\exp(-E/kT) - 1]\ dy}{\int_0^\infty [\exp(-E/kT) - 1]\ dy} \tag{18b}$$

K is a measurable parameter, since Γ can be determined as a function of C_∞ at equilibrium. Although L* is not directly measurable, it has the same order of magnitude as L.[18]

The applicability of continuum mechanics could be questioned if L* < 10Å, but thermodynamics leaves no doubt that a solute gradient will cause flow. In addition, there are two other implicit assumptions: The surface is smooth, and there are no kinetic barriers to the adsorption and desorption of solute.

Equation (17) shows the importance of the diffuseness of the interfacial layer. Even though K may be large, if the solute were actually adsorbed on the surface rather than in a diffuse layer then L* and U_{rel} vanish. It is not enough for the adsorption to be strong; the adsorbed layer must extend several solute diameters away from the surface to achieve meaningful velocities.

Flow Caused by Electrolyte Gradients

If the solute dissociates into ions, the analysis of stress and flow within the interfacial region is more complex because two species must be accounted for as well as the local electrostatic potential. However, in the case of electrolytes, the thickness of the interfacial region is known a priori:

$$L = \kappa^{1} = (\epsilon kT/8\pi z^2 e^2 C_\infty)^{\frac{1}{2}} \tag{19}$$

where κ is the Debye screening parameter that appears in equilibrium double-layer theory. We limit our discussion to electrolytes where cation and anion have the same charge number (z).

Under equilibrium conditions the ion concentrations at distances of κ^{-1} or less from a charged surface differ from their bulk values. The ion distributions in this region are

$$C_{\pm} = C_\infty \exp[\mp ze(\Psi-\Psi_\infty)/kT] \tag{20}$$

where the upper and lower signs refer to cation and anion, respectively. In diffuse double-layer theory (i.e., the Gouy-Chapman model[9]) Eq. (20) is used to compute the space charge in Poisson's equation (the continuum representation of Coulomb's law). The result is the Poisson-Boltzmann equation which has the following solution:

$$\begin{aligned} \tanh(u/4) &= \gamma \exp(-\kappa y) \qquad (21)\\ u &= ze(\Psi-\Psi_\infty)/kT \\ \gamma &= \tanh(u_s/4) \end{aligned}$$

where u_s is the potential at the surface (i.e., the "zeta potential"), rendered in dimensionless form. The pressure variation within the interfacial region is obtained by balancing the normal component of the pressure gradient with that component of the electrostatic body forces acting on a fluid element:

$$\frac{dp}{dy} + ze\ (C_+ - C_-)\ \frac{d\Psi}{dy} = 0 \quad . \tag{22}$$

Integration produces the following result when (20) is used:

$$p-p_\infty = 2C_\infty kT\ [\cosh(u) - 1] \quad . \tag{23}$$

Because cosh(u)-1 is an even function and always positive, $p-p_\infty > 0$ within the double layer no matter what the sign of u(y).

If the bulk concentration C_∞ changes gradually enough along a parallel to the surface, (23) still can be applied locally, but p now depends on x; $\partial p/\partial x$ is not balanced by the x-component of the electrostatic body force. Using (20), (23) and the definition of u, the net tangential force per volume acting on fluid elements is found to be:

$$\frac{\partial p}{\partial x} + ze(C_+-C_-)\frac{\partial \Psi}{\partial x} = 2kT\,[\cosh(u)-1]\,\frac{dC_\infty}{dx} + ze(C_+-C_-)\frac{d\Psi_\infty}{dx} \qquad (24)$$

If the cation and anion diffusion coefficients (D_+ and D_-) are not identical, the gradient in concentration of salt in the bulk fluid gives rise to a "diffusion current," since one ion diffuses more rapidly than the other. To prevent a continuous separation of charge, an electric field spontaneously arises in the bulk to produce an "electric current" which exactly balances the diffusion current. The necessary electric field is given by:[20]

$$-\frac{d\Psi_\infty}{dx} = \beta\,\frac{kT}{ze}\,\frac{d\,\ell n\,C_\infty}{dx} \qquad (25)$$

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

Generally, the right-hand-side of (24) is nonzero, so the fluid elements accelerate until viscous stresses bring the forces into balance. Equating the right-hand-side of (24) with $\eta\,\frac{d^2v_x}{dy^2}$ and using (20) to express C_+-C_- in terms of u yields:

$$\eta\,\frac{d^2v_x}{dy^2} = 2kT\,[(\cosh(u) - 1) + \beta\,\sinh(u)]\,\frac{dC_\infty}{dx} \qquad (26)$$

The second term on the right-hand-side of (24) or (26) results from the induced electric field acting on the space charge in the double layer; this gives rise to the "electrophoretic" contribution to relative motion between fluid and solid. The first term is associated with net adsorption of the electrolyte:

$$\Gamma = \int_0^\infty [C_+ + C_- - 2C_\infty]\ dy = 2C_\infty \int_0^\infty [\cosh(u) - 1]\ dy \qquad (27)$$

and produces the "chemiphoretic" contribution. After substituting (21), the integration of (26) gives the relative velocity between fluid and solid:

$$U_{rel} = -\frac{\epsilon}{4\pi\eta}\left(\frac{kT}{ze}\right)[\beta\ u_s - 2\ \ell n\ (1-\gamma^2)]\ \frac{d\ \ell n\ C_\infty}{dx} \qquad (28)$$

where γ is given under (21). Note that chemiphoresis [the second term in (28)] always tends to move the fluid toward lower C_∞ but electrophoresis could cause motion in either direction depending on the sign of the product βu_s. It appears from (28) that the relative fluid velocity is proportional to $d\ell n C_\infty/dx$ rather than to dC_∞/dx, but this is not necessarily so since u_s, and hence γ, could also depend on C_∞.

PARTICLE MOVEMENT: INFINITESIMALLY THIN INTERFACIAL LAYERS

In the previous section we examined fluid motion generated by a solute concentration gradient directed parallel to an infinite planar, solid surface which was considered stationary. These results can be applied to large particles of arbitrary shape to obtain the diffusiophoretic velocity in a stagnant fluid. By "large" we mean a particle whose surface appears flat on the local scale of the interfacial region. As shown in the next section, this means that the mean radius of curvature of the particle surface is everywhere much larger than both L and the adsorption length K.

Outside the interfacial region (y >> L) the solute gradient generates no force on the fluid. Consider an imaginary boundary $\mathcal{S}_o$ which encloses the particle but is never closer than several L from the particle surface. Because no forces act on the fluid outside $\mathcal{S}_o$, the velocity field $\underline{v}$ must be of such form that the net fluid force acting on $\mathcal{S}_o$ from the outside is zero. (Note that the coordinate system moves with the particle, so $\underline{v} \to -\underline{U}$ at great distances from the particle, where $\underline{U}$ is the particle velocity in a laboratory-fixed coordinate system.) For an incompressible Newtonian fluid this zero-force constraint is written as

$$\iint_{\mathcal{S}_o} \underline{n} \cdot \underline{\underline{\sigma}} \, dS = \underline{0} \quad , \quad \underline{\underline{\sigma}} = - p\underline{\underline{I}} + \eta \left[\nabla \underline{v} + (\nabla \underline{v})^T \right] \tag{29}$$

where the unit normal $\underline{n}$ points out of the region enclosed by $\mathcal{S}_o$. Velocity fields satisfying (29) but having viscous character inside the interfacial region are called "phoretic flows." Other examples of this type of flow are electrophoresis of charged particles[12,25] and vesicle movement in an osmotic gradient.[26]

We now demonstrate that the results for a flat surface, Eqs. (17) and (28), also give the diffusiophoretic velocity of a rigid particle of arbitrary shape in the limit that both L/a and K/a tend to zero, where $\underline{a}$ is the mean radius of curvature of the particle. Suppose $C_\infty(\underline{x})$ is the undisturbed solute concentration at position $\underline{x}$ in laboratory-fixed coordinates, and $\underline{x}_o$ is the instantaneous position of the center of the particle and $\underline{r}=\underline{x}-\underline{x}_o$. Outside the thin interfacial region the concentration $C(\underline{r})$ must satisfy the conservation equation:

$$\nabla^2 C = 0 \tag{30}$$

$$r \to \infty \qquad C \to C_\infty(\underline{x}_o) + \underline{r} \cdot \nabla C_\infty \tag*{(i)}$$

Convection of solute can be neglected in (30) due to the small velocities typically expected. As the surface of the particle is approached, but staying outside the thin interfacial region, the flux of solute normal to the surface approaches zero. In the limit we have

$$\text{on } \mathcal{S}_p^+ : \qquad \underline{n} \cdot \nabla C = 0 \tag*{(ii)}$$

where the + on $\mathcal{S}_p$ emphasizes that this condition applies immediately outside of the interfacial region. Condition (ii) says that the interfacial region is so thin that it cannot accommodate a finite flux of solute into it from the outside region.

The velocity field in the $\underline{r}$ coordinate system must satisfy the Stokes equations,

$$\eta\nabla^2\underline{v} = \nabla p \qquad (31)$$
$$\nabla\cdot\underline{v} = 0$$
$$r \to \infty : \quad \underline{v} \to -\underline{U} \qquad (\mathrm{i})$$

where $\underline{U}$ is the particle velocity. $\underline{v}$ must also satisfy the phoretic condition (29). A field which satisfies these equations is

$$\underline{v} = -\nabla\phi \qquad (32)$$

$$\nabla^2\phi = 0 \qquad (33)$$
$$r \to \infty : \quad \nabla\phi \to \underline{U} \qquad (\mathrm{i})$$

where ϕ is a scalar function of $\underline{r}$. By the same arguments used for the solute, the fluid cannot enter the thin interfacial region:

$$\text{on } \mathscr{S}_p^+ : \quad \underline{n}\cdot\nabla\phi = 0 \qquad (\mathrm{ii})$$

Note from (30) and (33) that C and ϕ must satisfy the same differential equation and very similar boundary conditions [(30-i) could be replaced by $\nabla C \to \nabla C_\infty$]. To fully connect the two variables we must consider the solute flux and fluid velocity directed parallel to the surface $\mathscr{S}_p^+$. If we use the results of the preceding section there obtains

$$\text{on } \mathscr{S}_p^+ : \quad \underline{v} = \underline{U}_{rel} = b\,\nabla C \qquad (34)$$

The coefficient b is determined from (17) for non-electrolytes and (28) for electrolytes. Combining (34) with boundary conditions (30-ii) and (33-ii) we have

$$\text{on } \mathscr{S}_p^+ : \quad \nabla\phi = -b\,\nabla C \qquad (35)$$

By examining (30), (33) and (35) one finds that a new variable $Y \equiv \phi + bC$ must satisfy

$$\nabla^2 Y = 0 \qquad (36)$$

$$\text{on } \mathscr{S}_p^+ : \quad \nabla Y = \underline{0}$$
$$r \to \infty : \quad \nabla Y \to \underline{U} + b\,\nabla C_\infty$$

These equations overspecify Y unless $\underline{U} = -b\nabla C_\infty$; then the solution is Y=0 everywhere. Thus the relationship between the velocity and the concentration gradient in the bulk turns out to be identical to (34) which relates the same quantities at any point on the outer boundary of the interfacial region. This gives the following expressions for particle velocity:

Non-Electrolyte:
(from (17))

$$\underline{U}_o = \frac{L^*K\ kT}{\eta} \qquad (37)$$

Electrolyte:
(from (28))

$$\underline{U}_o = \frac{\epsilon}{4\pi\eta}\left(\frac{kT}{ze}\right)^2 [\beta u_s - 2\ \ell n\ (1-\gamma^2)]\ \nabla\ \ell n\ C_\infty \qquad (38)$$

The subscript "o" emphasizes that these results are only valid in the limit K/a → 0 and L/a → 0.

The above analysis shows that $\underline{U}_o$ is independent of particle size and shape. Interfacial properties control the velocity for a given solute gradient. In the case of non-electrolytes, K can be determined experimentally by equilibrium adsorption studies, but there seems to be no direct method of determining L* from an independent experimental observation. For electrolytes all that is needed is the dimensionless zeta potential (u_s) which can be determined experimentally by electrophoresis or sedimentation potential, or theoretically from a knowledge of the density of charge groups on the particle surface. As noted in the previous section, u_s (and hence γ) could depend on C_∞ so that $\underline{U}_o$ is not necessarily proportional to $\nabla \ell n C_\infty$.

An interesting feature of the electrolyte result is that a particle could move either up or down the solute gradient. The chemiphoresis term $-2\ \ell n(1-\gamma^2)$ is always positive, tending to pull the particle toward higher solute concentration. On the other hand, β and u_s are independent parameters; if $\beta u_s > 0$ the electrophoretic effect augments the chemiphoretic effect by pulling the particle toward higher solute concentrations, but if $\beta u_s < 0$ then the electrophoretic effect tends to move the particle toward lower solute concentration. A map giving the direction of net motion based on Eq. (38) is shown in Figure 3.

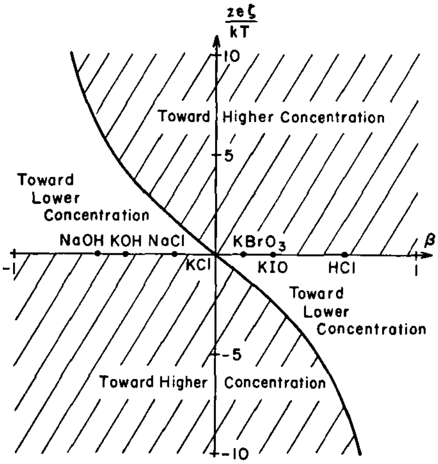

FIGURE 3
Map showing the direction of net migration for $\kappa a=\infty$.

Because β is a parameter of the solute only, the direction and speed of the particle can be adjusted by appropriate selection of the electrolyte species, assuming it has little effect on particle zeta potential. For example, consider a charged particle having $u_s = +1$ in an aqueous solution at 25°C with a gradient $|\nabla \ell n C_\infty| = 230\ cm^{-1}$ (i.e., an order of magnitude change in C_∞ over a distance of 0.1 mm). For two different electrolytes (38) gives

KCl (β = -0.0067*) U_o = + 1.43 μm/sec
NaCl (β = -0.195*) U_o = - 0.84 μm/sec

Thus, the same particle which migrates toward regions of <u>higher</u> KCl concentration would migrate toward <u>lower</u> NaCl concentration. If the particle were negatively charged ($u_s < 0$), it would migrate toward higher concentrations of both KCl and NaCl.

At this point we should re-examine the Marangoni analysis[13] in an effort to determine how it relates to diffusiophoresis. We have solved the system of equations describing a spherical fluid

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*Estimated from limiting ionic conductance.

drop of radius $\underline{a}$ placed in a non-electrolyte gradient, assuming a thin interfacial region ($K/a \to 0$) and no solute can enter the fluid inside the drop.[18] The result for the drop velocity is

$$\underline{U}_o = \left[\frac{3\eta_i L^* + \eta a}{3\eta_i + 2\eta} \right] \frac{K\, kT}{\eta} \nabla C_\infty \tag{39}$$

Because $L^* \ll a$, the term accounting for diffuseness of the interfacial region is negligible when $\eta_i \sim \eta$ so that (39) agrees with (16) under this condition. As the drop is made more viscous, however, the diffuseness becomes more important and must be considered when $\eta_i \gtrsim \eta\, a/L^*$. Equation (39) reconciles diffusiophoresis with Marangoni motion, giving (16) when the interior is fluid and (37) as the interior becomes rigid. Note that it is the ratio of η_i/η which is important. For example, if $L^*/a = 10^{-3}$ then a small drop of oil ($\eta_i \gtrsim 10^{-1}$ poise) in air is essentially "rigid" and Eq. (37) applies.

The analysis leading to (37) and (38) was for a single particle. If a number of particles are dispersed in a finite volume of liquid, one might ask "at what particle concentration do particle-particle interactions affect these results?" The problem examined here, in the limit $K/a \to 0$, is mathematically identical to electrophoresis when $\kappa a \to \infty$. The hydrodynamic interaction between pairs of particles, as well as the pair effect on the solute gradient, falls off as r^{-3} where r is the distance between particles. From the result for the electrophoresis of a suspension,[27] we expect the diffusiophoretic velocity of particles at finite volume fraction φ to be

$$\underline{U} = \underline{U}_o \left[1 - \varphi + O(\varphi^2)\right] \tag{40}$$

where $\underline{U}_o$ is determined from (37) or (38). Thus, only if the suspension has a volume fraction greater than a few percent does one have to correct for the finite concentration of particles.

FINITE INTERFACIAL LAYERS

In the previous section we considered interfacial layers

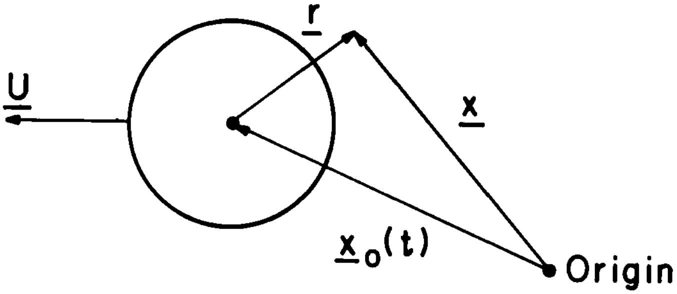

FIGURE 4
Schematic showing relationship between moving and stationary coordinates.

which are very thin compared to particle dimensions, but no criterion was offered for the restriction "very thin." Thus, the results (37) and (38) must be considered limiting cases for which the range of validity is not known. In this section we consider the effect of finite values of λ for spherical particles, where λ is the ratio of the interfacial layer thickness (L or κ^{-1}) to the particle radius. Only a summary of the analysis for finite λ is presented here; more details are available elsewhere.[18,19]

Non-Electrolytes

The problem of finding the particle velocity is most easily solved by working with a coordinate system ($\underline{r}$) which is centered on and moves with the particle, as shown in Figure 4. Let $C_\infty(\underline{x})$ be the undisturbed solute concentration field which would exist in the absence of the particle, and let α be $|\nabla C_\infty|$ evaluated at the particle's center $\underline{x}=\underline{x}_o$. As the particle migrates, its environment and velocity may change; however if the migration speed is slow enough, a quasi-steady state is achieved. The analysis below parallels that presented in Ref. 18, except that convective transport of solute is included.

Conservation of solute is expressed through the following dimensionless equation:

$$\nabla^2 C^* + \nabla \cdot (C^* \nabla \Phi) = Pe_1\, \underline{v} \cdot \nabla e^{-\Phi} + Pe_2 \left[\underline{v} \cdot \nabla C^* + \underline{\tilde{U}} e^{-\Phi}\right] \quad (41)$$

$$\rho = 1 : \qquad \frac{\partial C^*}{\partial \rho} + C^* \frac{\partial \Phi}{\partial \rho} = 0$$

$$\rho \to \infty : \qquad C^* \to \rho \cos\theta$$

$\Phi \equiv E/kT$ is the dimensionless solute-surface energy of interaction, while C^* is a dimensionless perturbation in solute concentration,

$$C^* = \frac{C - C_\infty(\underline{x}_o)\exp(-\Phi)}{\alpha a} \tag{42}$$

$\underline{v}$ and $\underline{\tilde{U}}$ are the local fluid velocity and particle velocity, both made dimensionless by U_o given in (37), and $\rho = r/a$ where a is the particle radius. The two Peclet numbers are defined as

$$Pe_1 = \frac{C_\infty(\underline{x}_o)\ L^*K\ kT}{D\eta} \quad , \quad Pe_2 = \frac{\alpha a L^*K\ kT}{D\eta} \tag{43}$$

Two such parameters are needed because there are two characteristic values of concentration, $C_\infty(\underline{x}_o)$ and αa. Sample calculations show $Pe_2 \ll 1$ but $Pe_1 \sim O(1)$, and hence Pe_1 could be an important parameter in some situations. The difference in magnitude between the two Peclet numbers arises because $C_\infty \gg \alpha a$ in general.[*]

Stokes' equation for the velocity field $\underline{v}$ is solved using a dimensionless stream function $\tilde{\Psi}(\rho,\theta)$ which automatically satisfies the continuity of mass. The momentum equation must be augmented by the addition of a body-force term equal to $-C\nabla E$ [see Eq. (13)]. After the curl of the momentum equation is taken to eliminate the pressure variable and the equation is rendered dimensionless, the result is

$$E^4(\tilde{\Psi}) = \frac{d\Phi}{d\rho}\frac{\partial C^*}{\partial \theta}\sin\theta \tag{44}$$

$$\text{where} \quad E^2 = \frac{\partial}{\partial \rho^2} + \frac{\sin\theta}{\rho^2}\frac{\partial}{\partial\theta}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\right)$$

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[*] If αa were not smaller than C_∞, the solute concentration would be negative on the low-concentration side of the particle.

$$\rho = 1 : \quad \tilde{\Psi} = 0 \ , \ \frac{\partial \tilde{\Psi}}{\partial \rho} = 0 \tag{i}$$

$$\rho \to \infty : \quad \tilde{\Psi} \to \frac{1}{2} \tilde{U} \rho^2 \sin^2\theta \tag{ii}$$

Condition (i) says $\underline{v}=\underline{0}$ on the particle surface (remember that the coordinate system moves with the particle), while (ii) says $\underline{v} \to -\tilde{\underline{U}}$ far from the particle. To determine $\tilde{\underline{U}}$ we use the phoretic condition (29), which requires the stream function to satisfy[28]

$$\lim_{\rho \to \infty} \left[\frac{\tilde{\Psi} - \frac{1}{2} \tilde{U} \rho^2 \sin^2\theta}{\rho} \right] = 0 \ . \tag{iii}$$

Note that to derive (44) the solute-particle potential Φ was assumed to be independent of θ (i.e., the surface of the particle is homogeneous) and solute concentration.

Because the range of Φ is quite short compared to the particle radius, the above equations are very different inside the interfacial region ($\rho-1 \lesssim \lambda$, where $\lambda=L/a$) compared to the outer region ($\rho-1 \gg \lambda$). This difference suggests that the solution to (41) and (44) should be approached through a method of matched asymptotic expansions. The variable $y=(\rho-1)/\lambda$ is used within the interfacial region ($y \sim O(1)$), while ρ is used in the outer region. The <u>dimensional</u> particle velocity is expanded in powers of λ as

$$\underline{U} = \underline{U}_0 \, [1 + c_1\lambda + c_2\lambda^2 + \dots] \tag{45}$$

where $\underline{U}_0$ is given by (37) and is independent of Pe_1 or Pe_2, but the coefficients c_n could be functions of the Peclet numbers. For negligibly small Peclet numbers the solution to (41) and (44) gives[18]

$$Pe_1 = Pe_2 = 0 : \quad c_1 = -\left[\frac{K}{L} + \frac{H}{L} \right] \tag{46}$$

where K is given by (9) and

$$H = \frac{L}{2} \, \frac{\int_0^\infty y^2 \, [\exp(-\Phi) - 1] \, dy}{\int_0^\infty y \, [\exp(-\Phi) - 1] \, dy}$$

In general, $H \approx L \ll K$ so that (45)-(46) can be approximated by:

$$Pe_1 = Pe_2 = 0 : \qquad \underline{U} = \underline{U}_o \left[1 - \frac{K}{a} + O(\lambda^2) \right] . \tag{47}$$

Thus the first correction for particle curvature is $O(K/a)$ rather than $O(\lambda)$; that is, "thinness" of the interfacial region is determined by K, not L. In other words, (37) gives the particle velocity only when $K/a \ll 1$, which could place severe restrictions on how large *a* must be for systems with K values of order 1μm or larger.

In problems[14,26] with a mathematical structure similar to that above, the dependence on Pe_2 is $O(Pe_2^2)$ with a coefficient near unity. Sample calculations indicate $Pe_2 \ll 10^{-2}$, so that the assumption $Pe_2=0$ is probably reasonable for most situations. On the other hand Pe_1 could be one or larger so its effect should be considered. To do this one must return to the analysis of (41) in the inner region at $O(\lambda^2)$. Referring to Eq. (2.18) of Anderson *et al.*[18], the function Λ_2 is modified by adding the term

$$Pe_1 \, \lambda^{-1} \, v^i_{r1} \, (\cos\theta)^{-1} \tag{48}$$

where v^i_{r1} is the $O(\lambda)$ contribution (the leading non-zero term) to the r component of fluid velocity in the inner region and is determined using the $O(\lambda^0)$ contribution to v^i_θ [v_x in Eq. (16)] and the continuity equation:

$$v^i_{r1} = - 3 \, \frac{\lambda \cos\theta}{A} \int_0^y (y-y') \, dy' \int_{y'}^{\theta} [\exp(-\Phi(y^*)) - 1] \, dy^* \tag{49}$$

$$(A = L^*K/L^2)$$

Proceeding with the analysis as described by Anderson *et al.*[18] and matching inner to outer solutions gives a coefficient b_1 which has an additional term proportional to Pe_1. Using this augmented b_1 in the analysis of (44) gives the following dimensional result:

$$\underline{U} = \underline{U}_o \left[1 - (1 + \upsilon \, Pe_1) \frac{K}{a} + O(\lambda^2) \right] \tag{50}$$

$$\upsilon = \frac{1}{L^*K^2}\int_0^\infty dy \left\{\int_y^\infty [\exp(-\Phi(y^*)) - 1]\right\}^2$$

where y is now dimensional and equal to r–a, i.e., the distance from the particle surface. υ equals 1/3 if $\Phi(y)$ is a step function and 1/2 if Φ is a Dirac function.

A reduction in speed by convective transport of solute can be rationalized as follows. As the particle moves through the solution, solute builds up on the forward pole ($\theta=0$) at a rate $\sim UC_\infty(\underline{x}_o)$, while solute is depleted at the other pole ($\theta=\pi$) at the same rate. Due to the force $-E'(y)$ by the particle on each solute molecule, this excess solute creates an additional pressure over the front hemisphere which opposes its motion forward.

According to (50), which can be applied when $Pe_2 \ll 1$ and $H \ll K$, there are three groups of parameters which control the particle velocity induced by a gradient: L^*K, K/a, and υPe_1, where the appropriate definitions of parameters are given by Eqs. (18) and (43). The range of validity of (50) can probably be extended to larger values of K/a by using the Padé approximant,

$$\underline{U} = \underline{U}_o \left[1 + (1+\upsilon Pe_1)\frac{K}{a}\right]^{-1}$$

Electrolytes

Except for the differences already noted in the analysis for infinitesimally thin interfacial layer, the electrolyte problem with finite interfacial layers is very similar to that for nonelectrolytes. Consequently the analysis of Prieve *et al.*[19] for electrolytes (which is more cumbersome than that for nonelectrolytes) will not be outlined here, but one intermediate result is worthy of note. Through a judicious combination of the dependent variables, the perturbation in the potential field u, caused by the macroscopic concentration gradient, can be eliminated from the problem. In particular, the boundary condition for the perturbation in u at r=a is not used in predicting the velocity. Thus we do not need to specify how the surface charge or zeta potential will change in response to a change in ionic strength; the only property of the charged interface which must be known to predict the velocity is its zeta potential in a uniform solution of concentration $C_\infty(\underline{x}_0)$.

The particle velocity induced by a macroscopic gradient in concentration of a z-z electrolyte is given by:[19]

$$\underline{U} = \frac{\epsilon}{4\pi\eta}\left(\frac{kT}{ze}\right)^2 \left\{\beta u_s(1-3\lambda) + \frac{1}{8}u_s^2\left(1 - \frac{21}{2}\lambda\right)\right\} \nabla \ln C_\infty \qquad (51)$$

with an error of $O(\lambda^2)$ and $O(u_s^3)$. Note that in the limit $\lambda=0$ the above expression agrees with (38). The effect of finite λ is to retard the particle velocity. The correction -3λ for the electrophoretic component is identical to the $O(\lambda)$ correction at $|u_s| < 1$ for electrophoresis.[2]

A superficial comparison between (51) and (50) would seem to indicate that the $O(\lambda)$ correction for electrolytes is considerably weaker than for non-electrolytes. However, we must keep in mind that (51) assumes $|u_s| < 1$ for which the adsorption length is small $[K=O(\kappa^{-1})]$.

Roman[32] has obtained a numerical solution for the chemiphoretic contribution using arbitrary values of u_s and λ. In the limit $\lambda \to 0$, his results confirm both (38) and (51). In the other extreme ($\lambda \to \infty$) where the particle behaves like a point charge, the chemiphoretic velocity becomes vanishingly small. The reduction in speed as λ becomes large is already evident in the $-21\lambda/2$ term of (51). Finally, when $|u_s|$ is increased holding λ fixed, Roman observed that the chemiphoretic velocity first displays a maximum value before decaying to zero as $|u_s| \to \infty$. This might be rationalized by noting that as $|u_s|$ increases, the adsorption length K also increases. If $|u_s|$ is large enough, K/a might be large even though $\lambda << 1$: apparently the particle behaves like a point charge (which has vanishingly small chemiphoretic velocity) when either $K/a \to \infty$ or $\lambda \to \infty$.

The $O(\lambda)$ correction given by (51) is valid through $O(u_s^2)$. Prieve et al.[19] also computed the $O(\lambda)$ correction for arbitrary u_s. For larger values of u_s, the $O(\lambda)$ correction grows exponentially with $|u_s|$.

EXPERIMENTAL OBSERVATIONS

As early as the 1920's, rubber gloves and other articles of rubberized clothing were made from natural latex by a process called "coacervate dipping".[33] In this process, a form is first coated with salt crystals or a film of a concentrated salt solution and then immersed in a concentrated dispersion of latex. After a brief exposure, the form is coated by coagulated latex. A simple explanation is that the high concentration of salt induces localized coagulation at the surface of the form. However, to form a deposit of a given thickness, a region several times thicker than this deposit must be depleted of latex. Simple diffusion of latex particles cannot explain the high rate of deposition observed. Some other transport mechanism is responsible. Derjaguin et al.[1] suggested diffusiophoresis as the mechanism.

Dukhin and Zueva[34] investigated the deposition process experimentally by using a cellophane membrane to separate a $CaCl_2$ solution from the latex. Diffusion of the salt through the porous membrane induces deposition of the latex. This arrangement allows both the salt and latex concentrations to be varied. Although they report difficulties with gravimetric determination of the rate of deposition, they were able to detect the existence of deposits visually. The formation of deposits from very dilute dispersions (0.1 wt % solids) confirms the existence of some transport mechanism which concentrates the latex at the surface. They observed that, below some critical concentration of salt, no deposit is obtained. This critical salt concentration increases with increasing latex concentration. They concluded that this behavior resulted from ions contained in the serum of the latex, which either diffuse countercurrently to the $CaCl_2$ and reverse the direction of diffusiophoresis, or chemically react with the $CaCl_2$ and precipitate it from solution. Derjaguin et al.[35] have performed similar experiments in which the effect of adding electrolyte to the latex dispersion was studied.

Lin and Prieve[36,37] have reported gravimetric measurements of the rate of deposition of colloidal latex onto a porous polycarbonate membrane through which a salt diffuses. They measured the rate of deposition of either anionic or cationic latex (0.5 wt % solids), induced by diffusion of any one of a dozen different electrolytes, and correlated their results with the "diffusion potential" measured across the membrane. They examined the effect of the concentration of the salt solution placed on the salt-side of the membrane, the effect of any supporting electrolyte added to the serum of the latex, and the effect of agitation rate. All of their results are consistent with a model in which the rate is determined by the electrophoretic migration of the latex particles in the electric field induced at the outer edge of the deposit by the diffusion of salt. In these experiments, the addition of a second salt in equal concentrations on both sides of the membrane decreased the rate of deposition induced by diffusion of the first salt by weakening the electric field. This effect could also lead to a critical concentration of the first salt required for deposition as reported by Dukhin and Zueva.[34]

Microscopic observations of single particles moving in a salt gradient have also been attempted. Derjaguin et al.[38] looked downward along a tangent to a vertical cellophane membrane to observe anionic latex particles moving toward or away from the membrane as salt diffused through it in an unsteady manner. Placing a solution of KCl or $CaCl_2$ on the opposite side of the membrane from the latex, the latex particles were induced to migrate toward the membrane; whereas placing distilled water on one side of the membrane and the salt and latex on the other side, the latex particles moved away from the membrane. Velocities up to 1μm/s were observed in $CaCl_2$, but they were considerably smaller in KCl. The direction in which migration occurred in each of these experiments is consistent with that predicted by Eq. (38). A lower speed is also expected for KCl ($\beta = 0$) since the electrophoretic contribution (which, in the case of $CaCl_2$, acts in concert with the chemiphoretic contribution) is vanishingly small. Although Derjaguin et al.[38] concluded that KCl gradients do induce migration of latex particles, Lin and Prieve[36,37] saw no evidence of a significant deposit in the absence of an induced electric field.

Natural convection is one source of error in local microscopic observation. If salt is diffusing through the membrane into the latex, then the layer of solution next to the membrane on the latex side will be more dense than the solution far away. This generates downward motion across the face of the membrane and draws fluid toward the membrane at the top of the cell where the microscopic observations of particle motion are made. Conversely, if salt diffuses from the latex into the membrane, the solution next to the membrane will be less dense and convection will occur in the opposite direction. Unfortunately, in all the cases examined by Derjaguin et al.[38] the observed particle motion occurs in a direction which coincides with that of natural convection. Another source of error is osmotic flow through the membrane which is expected as a result of the concentration difference across it. For such an experiment to be compelling, the effect of natural convection and osmotic flow must be assessed independently of diffusiophoresis.

Carr[39] microscopically observed the motion of 3μm anionic latex particles in a sealed capillary whose axis was oriented vertically. An unsteady salt gradient was created by the dissolution of a salt crystal, introduced at the bottom end before sealing. With the more dense solution on the bottom, natural convection is avoided. Although sedimentation is now important, this contribution to particle motion can be independently assessed by observing the particle before the salt has had time to diffuse to its vicinity. When NaCl ($\beta < 0$) was used as the salt, the concentration gradient attracted the particles toward the crystal with a speed considerably above that due to sedimentation; whereas particles from the same latex were repelled from a crystal of KIO_3 ($\beta > 0$). Results with KCl or KNO_3 ($\beta \approx 0$) were inconclusive because a volume change upon dissolution ruptured the seal.

APPLICATIONS

Perhaps the oldest commercial process in which diffusiophoresis of hydrosols is known to be involved is "coacervate dipping",[33] which was described in the previous section. Several variants of this process, which is used to apply latex coatings, have been assigned other names such as "coagulant dip," the "Anode process" or the "US process".[40]

A more recent process is Autophoretic® deposition, which is currently used to apply the first layer of paint on automobile frames and other metal massware.[41] Instead of applying a film of salt on the metal prior to immersion in the latex, an acid and an oxidizing agent are added to the latex. Dissolution of the iron in the steel during immersion produces ions which attract latex particles to the steel and cause local coagulation. Using a formulation containing latex (5 wt % solids), HF and H_2O_2, Prieve et al.[42] confirmed patent claims and observed that the rate of deposition was linked to the rate of dissolution of the metal. They subsequently showed that the same process was capable of coating other metals like zinc, whose salts do not cause flocculation of the latex.[43] They proposed migration of the negatively charged latex particles in the electric field induced in the boundary layer by dissolution of the metal as the rate-determining step for deposition. This mechanism was later confirmed by Smith and Prieve.[8] A similar process for depositing latex on copper has been investigated by Derjaguin et al.[44]

Another possible application is enhanced deep-bed filtration. Fowkes et al.[45] reported a significant enhancement in the coalescence of emulsions by packed beds when mixtures of grains from two metals were used as packing compared to beds having all grains composed of the same metal. In their studies, the grains were composed either of C, Al, or Fe. They explained the enhancement by observing that a difference in oxidation potential could arise across the solution separating two grains composed of different metals. This potential difference, which would attract charged droplets to one of the grains, is zero when the two grains are composed of the same material. Thus the process was named "bimetallic coalescence". In a series of experiments comparing the performance of a C bed or an Al bed with one having a mixture of the two grains, the mixed bed clarified the haze caused by the oil droplets much better than the C bed, but the Al bed performed almost as well as the mixed bed. In a second series, C, Fe and C/Fe beds were compared. Results similar to the first series were obtained except that a precipitate of $Fe(OH)_3$ accumulated in the bed, which clearly indicates dissolution of the metal has occurred.

An equally plausible mechanism is the diffusiophoretic migration of droplets to the dissolving metal grains. The difference in oxidation potential may serve to increase the dissolution of Fe or Al instead of directly causing a potential drop across the solution. Considering only the electrophoretic contribution to diffusiophoresis, the resulting average flux of particles to the surface of the grains is given by:

$$N_E = m\,E\,c_p = m(\Delta\psi)c_p\,\delta_s \quad , \tag{52}$$

where m is the electrophoretic mobility of the particles, c_p is their concentration in the interstitial fluid, $E = (\Delta\psi)/\delta_s$ is the electric field induced by the diffusion of the salt, and $\Delta\psi$ is the diffusion potential induced across the diffusion boundary layer of thickness δ_s. In the absence of diffusiophoresis, the deposition of sub-micron particles occurs mainly by convective diffusion, whose rate is given by:

$$N_D = D_p \frac{c_p}{\delta_p} \quad , \tag{53}$$

where D_p is the diffusion coefficient of particles and δ_p is the thickness of the boundary layer for the diffusion of particles. According to the Levich-Lighthill equation for convective diffusion to a sphere $\delta \propto D^{-1/3}$. Thus dividing (52) by (53) yields:

$$\frac{N_E}{N_D} = \frac{m(\Delta\psi)}{D_p} \frac{\delta_s}{\delta_p} = \frac{m(\Delta\psi)}{D_p} \left(\frac{D_p}{D_s} \right)^{1/3} \qquad (54)$$

Substituting some typical values ($m=10^{-4}$ cm^2-v^{-1}-s^{-1}, $\Delta\psi =$ 25mV, $D_p = 10^{-8}$ cm^2/s, and $D_s = 10^{-5}$ cm^2/s), this equation predicts an enhancement in filtration efficiency of 25 fold.

Ghosh and Brown[46] made quantitative measurements of efficiency of removal of oil from oil-in-water emulsions by deep beds packed with C, Al and/or Fe grains. They studied the effect of flow rate, bed depth, porosity as well as changes in efficiency with time as precipitate and oil accumulate in the bed. As usual for deep-bed filtration, the fraction of oil in the effluent was found to decay exponentially with the depth of the bed. This overall behavior is consistent with a local deposition rate of droplets onto the grains which is first order with respect to droplet concentration — as in (52) and (53). The proportionality constant in the exponent is called the "filter coefficient." If the local deposition rate is determined by the electric field, and if the electric field is the difference in oxidation potentials divided by some average interparticle spacing, then the filter coefficient would be inversely proportional to the flow rate through the bed. The experimental data plotted on log-log paper display a slope which is considerably less negative than -1, which suggests that the local electric field must increase with flowrate. Since δ_s in (52) is expected to shrink with increasing flowrate, electrophoretic migration of the droplets caused by dissolution of the metal grains is consistent with these observations.

Liberman et al.[47] repeated the measurements of Fowkes et al.[45] They confirmed the effectiveness of beds having mixtures of metal grains in removing oil droplets; however, they noted that some granular beds composed of a single metal are just as effective. They deduced that the potential difference across the interstitial solution between dissimilar grains is only 14mV compared to a difference in oxidation potentials of nearly 800mV. Filtration of dilute, submicron, polystyrene latexes by beds packed by mixtures of metal grains was also studied. Some mixtures were very effective while others were not. In addition to intimate mixtures of two types of grains, they also tried arranging the two types of grains in two layers. For a given pair of metals, nearly the same results were obtained in either configuration. This indicates that the distance separating the different metals is not important. Finally they conclude that in order to obtain a high efficiency of filtration, the metal grains must corrode. This correlation between deposition rate and metal dissolution rate was also found in the coating experiments of Smith and Prieve.[8,42,43] It provides additional evidence for a common mechanism.

If dissolution of metal is required for enhanced filtration, the grains of the bed will have a limited lifetime. If the enhancement by metal dissolution occurs because of an induced diffusion potential (the $\nabla\psi$ in Eq. (52)), then nonmetallic grains which promote diffusion of ions toward or away from their surface should also enhance filtration. For example, the countercurrent diffusion of ions which occurs within ion-exchange resin beads will induce a diffusion potential. Beds of ion-exchange beads can be easily regenerated, providing an almost unlimited lifetime. In a preliminary study, FitzPatrick et al.[48] showed that ion-exchange could enhance filtration of micron-sized latexes by up to five fold. Filtration of biological organisms in beds of ion-exchange resins is an important process in industrial fermentation. A review by Daniels[49] contains over 500 references.

SUMMARY

Diffusiophoresis is the locomotion of a rigid colloidal particle which is induced by a macroscopic gradient of solute concentration. In this paper we have reviewed both the theory and experiments on diffusiophoresis of hydrosols. In order for a solute gradient to induce motion, there must be some interaction (e.g. electrostatic or van der Waals) between any solute molecule and the colloidal particle. This might be manifested as physical adsorption of the solute into the interface between the particle and the solution. The interfacial region must extend a few solute diameters from the solid if the motion is to be measurable.

Derjaguin and his Soviet coworkers first recognized this phenomenon and first predicted the relative speed between the fluid and the solid in the simple geometry of a flat plate.[1,15] Their later experiments confirmed that migration of latex particles can be induced by salt gradients.[34,35] More recently, we extended the analysis to spherical particles of finite radius.[18,19] For both electrolytes and uncharged solutes, the leading term in a power series expansion of the speed (in terms of the ratio of the thickness of the interfacial region to the particle radius) is identical to Derjaguin's result for the flat plate. The second term in this expansion (the leading term of the correction for curvature) is negative; thus curvature tends to retard the particle's speed. To neglect curvature, the particle's radius must be much larger than the adsorption length as well as the thickness of the interfacial region. Prieve and Roman have numerically obtained a more general solution for the case of electrolytes.[32] Recent experiments with commercial latexes in salt gradients[8,36] can be entirely explained by electrophoresis in the induced electric field; chemiphoresis, the second contribution to locomotion, seems to be far less important in these systems.

Commercial applications of diffusiophoresis include processes for forming rubber gloves and paint films. Diffusiophoresis can also enhance the efficiency of deep-bed filtration. Since the direction of net migration is predicted to depend on the size and charge of the particle, diffusiophoresis might be applied to the analysis of particle mixtures. Finally, we might speculate that there is some relationship between chemotaxis of biological cells and diffusiophoresis.

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