

DIFFUSIOPHORESIS OF A WEAKLY CHARGED NONCONDUCTING SPHERE

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Based on the ionophoretic approach, we have solved the problem of diffusiophoresis of a weakly charged dielectric spherically-shaped colloidal particle in a multicomponent electrolyte solution for an arbitrary ratio between the particle radius and the thickness of the electrical double layer (EDL). We have calculated in explicit form the leading term of the expansion of the diffusiophoresis velocity in powers of the electrokinetic potential of the particle; this term is proportional to the square of the electrokinetic potential and the gradient of the ionic strength of the solution.

Over the past decade, the possibility has been discussed in the literature of intensification of transport of dissolved substances, particularly proteins [1, 2], through synthetic membranes as a result of special selection of the chemical composition of the solutions and creation of microion concentration gradients on the membrane. Theoretical analysis of this possibility for the model case of macroporous membranes [3] leads to the problem of the diffusiophoresis of protein macromolecules in a multicomponent solution. Such a formation of the problem stems from the universality of the diffusiophoresis phenomenon, first examined experimentally and theoretically in the work of B. V. Deryagin and his co-workers [4, 5, 15]. In this report, we give a solution to this problem [5] in the case when protein macromolecules are considered as weakly charged spherical colloidal particles whose radius is comparable with the thickness of the electrical double layer [7]. In this case, the ionophoretic approach is used [8-10], in terms of which the motion of the particle is represented as the algebraic sum of motions under the action of individual types of ions: ionophoretic motions.

Formulation of the Problem. Let us first consider the problem of the motion of a particle under the action of ions of a specified type i ($i = 1, \dots, n$). The initial equations for describing ionophoresis are derived in [9, 10]:

$$\begin{aligned} \operatorname{div}[e^{-z_i\varphi}(\nabla\mu_i - v_i/D_i)] &= 0 \\ \operatorname{div}v_i &= 0 \\ \eta\Delta v_i - \nabla p_i + f_i &= 0, \quad f_i = c_i(e^{-z_i\varphi} - 1)\nabla\mu_i \end{aligned} \tag{1}$$

Here η is the dynamic viscosity of the liquid, D_i is the diffusion coefficient for ions of type i , z_i is their algebraic valency (positive for cations and negative for anions), μ_i is the electrochemical potential, c_i is the volumetric concentration, v_i is the flow velocity of the liquid relative to the particle, p_i is the flow pressure, f_i is the flow force, φ is the equilibrium potential of the electrical double layer (EDL), measured in RT/F units. The boundary conditions on the surface of a nonconducting particle of radius a impermeable to the liquid, are

$$v_i|_{r=a} = 0, \quad \left.\frac{\partial\mu_i}{\partial r}\right|_{r=a} = 0 \tag{2}$$

As the boundary conditions at infinity, for the ionophoresis problem we need to specify a homogeneous gradient of the electrochemical potential for ions of the i -th type (unless otherwise stated, we omit the index indicating the type here and later) and the condition that the total force acting on the particle is equal to zero

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$$\frac{\partial \mu}{\partial r} \Big|_{r \rightarrow \infty} = B \cos \theta; \quad F \Big|_{r \rightarrow \infty} = 0 \quad (3)$$

here θ is the angle between the symmetry axis of the system and the radius vector r directed toward a given point from the center of the particle. The velocity field should be regular at infinity; the velocity of the liquid relative to the particle, homogeneous at infinity and taken with a negative sign, will in this case be the ionophoresis velocity.

Approximate Solution Method. Let us look for an approximate solution to the system of equations (1), assuming that the dimensionless potential φ of the electrical double layer is small. Such an approach has been developed in papers by Henry [11], Overbeek [12], and Booth [13] in the theory of electrophoresis, but it has not been previously applied in the theory of diffusiophoresis and ionophoresis.

Omitting the detailed description of the procedure for solving the equations obtained in this case, given in [5], let us write out the final formulas for the components of the ionophoresis velocity, proportional to the first and second power of the equilibrium EDL potential (symbolized by V_{iph_1} and V_{iph_2} , respectively):

$$V_{iph_1}(\varphi) = \frac{a^2 c z}{3\eta} B \int_1^\infty dx \varphi(x) f_1(x) \quad (4)$$

$$V_{iph_2}(\varphi) = \frac{a^2 c z^2}{9\eta} B \int_1^\infty dx \varphi(x) \left[T f_2(x) + \varphi(x) f_3(x) + \int_x^\infty dy \varphi(y) f_4(x, y) \right] \quad (5)$$

where

$$\begin{aligned} f_1(x) &= -2x^2 + 2x - 1/2x^2 + 1/2x^4 \\ f_2(x) &= -3(x-1/x)2x^3, \quad f_3(x) = x^2 + 1/x - 9/4x^2 + 1/4x^4 \\ f_4(x, y) &= 6x(1-x)/y^4 + 3y^3(x-1/x)/x^3 \\ T &= \int_1^\infty \varphi(x) f_T(x) dx, \quad f_T(x) = 2x^2 + x^{-4} \end{aligned}$$

(in formulas (4)-(5), the radial coordinate x is expressed in units of the particle radius a).

Structure of the Equilibrium Electrical Double Layer. In order to make practical use of formulas (4) and (5) for calculation of ionophoretic mobilities, we need to substitute in them the expressions for the equilibrium EDL potential for a weakly charged spherical particle with a double layer of arbitrary thickness. This expression should contain terms all the way up to quadratic with respect to the ζ potential inclusively (we will call the potential on the particle surface, measured in RT/\mathcal{F} units, the ζ potential). If the term linear in the ζ potential does not depend on the composition of the solution (depends only on its ionic strength), then the term which is quadratic with respect to the ζ potential also depends on the composition of the solution. In order to calculate these terms, let us rewrite the Poisson-Boltzmann equation

$$\Delta\varphi = -\frac{4\pi\mathcal{F}^2}{\epsilon RT} \sum_i c_i z_i e^{-z_i u} \quad (6)$$

with boundary conditions

$$\varphi|_{r=0} = \zeta, \quad \varphi|_{r \rightarrow \infty} = 0 \quad (7)$$

Making use of the smallness of the ζ potential, let us expand (6) in a series in powers of ζ :

$$\Delta\varphi = \kappa^2 (\varphi - \lambda\varphi^2/2)$$

where $\kappa^2 = 4\pi\mathcal{F}^2 \sum_i c_i z_i^2 / \epsilon RT$ is the square of the reciprocal Debye radius, and the parameter

$\lambda = \sum_i c_i z_i^3 / \sum_i c_i z_i^2$ can be called the asymmetry of the solution. Let us now expand φ in a series in powers of the ζ potential.

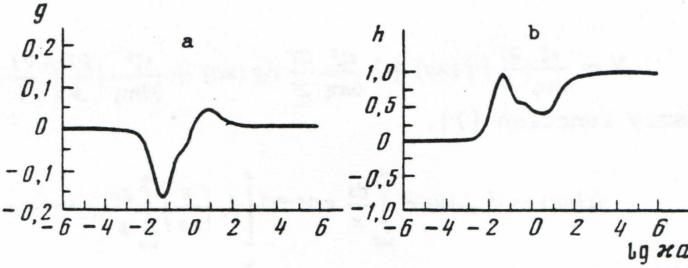


Fig. 1. Graphs of g (a) and h (b) as functions of the argument $\log x̑a$.

$$\varphi = \varphi_1 + \varphi_2 + \dots$$

and we obtain the following equation for the individual terms in the expansion:

$$\begin{aligned} \Delta\varphi_1 &= x^2\varphi_1 \\ \Delta\varphi_2 &= x^2(\varphi_2 - \lambda\varphi_1^2/2) \end{aligned} \quad (8)$$

The parameter φ_1 should satisfy the boundary conditions in (7), and φ_2 should satisfy the null boundary condition at both boundaries. The solutions to Eqs. (8) have the form

$$\varphi_1(x) = \zeta \frac{x\alpha}{x} e^{-(x-\alpha)} \quad (9)$$

$$\varphi_2(x) = T_1 \frac{e^{-x}}{x} - I_1(x) \frac{e^{-x}}{x} + I_2(x) \frac{e^{-x}}{x} \quad (10)$$

where

$$T_1 = I_1(\alpha) - e^{2\alpha} I_2(\alpha)$$

$$I_{1,2}(x) = \frac{1}{4} \int_x^\infty dy \lambda \varphi_1^2(y) y e^{\pm y}$$

and the variables x and y are measured in α^{-1} units. Now in order to obtain the ionophoretic mobility in a series in powers of the parameter ζ rather than in a series in powers of φ , we must regroup the terms in the expansion (4), (5). Substitution of φ_1 in (4) will give a single term, linear in ζ ; substitution of φ_2 in (4) and φ_1 in (5) will give terms quadratic in ζ .

Diffusiophoresis Velocity in a Multicomponent Solution. The velocity of a particle under the action of concentration gradients for all the solutes simultaneously is equal to the sum of the ionophoretic velocities, i.e., the terms of form (4) and (5), summed over all types of ions. We note that only the coefficients in front of the integrals (and not the integrals themselves) depend on the type of ions in these terms. Summation of these coefficients using the standard representation

$$\mathbf{B}_i = RT(\nabla c_i/c_i + z_i \nabla \varphi) \quad B_i = |\mathbf{B}_i|$$

gives

$$\begin{aligned} \sum_{i=1}^n \frac{a^2 c_i z_i \mathbf{B}_i}{3\eta} &= -\frac{\epsilon}{6\pi\eta} \frac{RT}{\mathcal{F}} E \frac{(\alpha)^2}{2} \\ \sum_{i=1}^n \frac{a^2 c_i z_i^2 \mathbf{B}_i}{9\eta} &= -\lambda \frac{\epsilon}{18\pi\eta} \frac{RT}{\mathcal{F}} E \frac{(\alpha)^2}{2} + \frac{\epsilon}{18\pi\eta} \left(\frac{RT}{\mathcal{F}} \right)^2 \frac{\nabla I}{I} \frac{(\alpha)^2}{2} \end{aligned}$$

Here $E = -RT\nabla\varphi/\mathcal{F}$ is the strength of the field of the diffusion potential of the ions, I is the ionic strength of the solution. The velocity of the particle to accuracy up to terms $O(\zeta^2)$ inclusively is rewritten in the form

$$V = \frac{\varepsilon \zeta}{6\pi\eta} \frac{RT}{F} Ef(xa) + \lambda \frac{\varepsilon \zeta^2}{6\pi\eta} \frac{RT}{F} Eg(xa) + \frac{\varepsilon \zeta^2}{32\pi\eta} \left(\frac{RT}{F}\right)^2 \frac{\nabla I}{I} h(xa) \quad (11)$$

where $f(xa)$ is the Henry function [7],

$$h(xa) = \left(\frac{8}{9}\right)(xa)^2 \int_{xa}^{\infty} \frac{dx}{x} e^{-(x-xa)} \left[f_2 \left(\frac{x}{xa}\right) \int_{xa}^{\infty} \frac{dy}{y} e^{-(y-xa)} \times \right. \\ \left. \times f_T \left(\frac{y}{xa}\right) + \frac{xa}{x} e^{-(x-xa)} f_3 \left(\frac{x}{xa}\right) + \int_x^{\infty} \frac{dy}{y} e^{-(y-xa)} f_4 \left(\frac{x}{xa}, \frac{y}{xa}\right) \right] \\ g(xa) = -(3/16)h(xa) + 1/8(xa)^3 \int_{xa}^{\infty} \frac{dx}{x} e^{-(x-xa)} f_1 \left(\frac{x}{xa}\right) e^{xa} \times \\ \times [Ei(-xa) - e^{2xa} Ei(-3xa) - Ei(-x) + e^{2x} Ei(-3x)]$$

We emphasize that expression (11) is valid in the case of a multicomponent solution of arbitrary composition. Its two terms, describing electrophoresis in the field of the diffusion potential of the ions, were calculated for the first time by Henry [11] and Overbeek [12]. Relative to the function h in the third term, previously it was only known that $h \rightarrow 1 - (21/2)(xa)^{-1}$ as $xa \rightarrow \infty$ [15, 16]. Asymptotic analysis of the expressions for the functions g and h shows that

$$g \approx \frac{9}{8xa}, \quad h \approx 1 - \frac{21}{2xa}, \quad xa \rightarrow \infty \\ g \approx \frac{xa}{6}, \quad h \approx \frac{4}{9}xa, \quad xa \rightarrow 0$$

The form of these functions for an arbitrary value of the argument is shown in Fig. 1.

The results obtained can be used to describe processes of protein transport in solutions and in porous diaphragms.

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