Diffusiophoresis of a charged toroidal polyelectrolyte
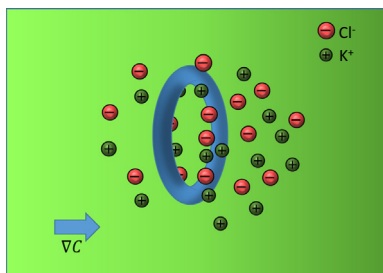
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GRAPHICAL ABSTRACT

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ABSTRACT

Considering recent application of concentration driven motion of charged nanoparticles in sensing technology, we model the diffusiophoresis of an isolated toroidal polyelectrolyte (PE) for the first time. Choosing an aqueous KCl solution for illustration, its behavior under various conditions is simulated by varying the double layer thickness, the size of toroid, and its softness and fixed charge density. We show that the behavior of the present PE can be different both quantitatively and qualitatively from that of the corresponding spherical PE. This arises from the competition of the hydrodynamic force and the electric force acting on a PE. The geometry and the nature of a PE can also influence appreciably its behavior, yielding complicated and interesting results.

1. Introduction

Diffusiophoresis, a solute concentration gradient driven phenomenon, has been applied in many areas of practical significance including, for example, separation [1,2], coating [3–6], purification [7], and scavenging [8,9]. It also plays a role in modern nanotechnology based applications such as DNA sensing [10], drawing the attention of researchers in various fields, recently. Chou [11] and Wanunu et al. [12], for instance, showed that the efficiency of the applied electric field based DNA sensing can be improved appreciably by applying simultaneously a salt concentration gradient. Since particles are driven by a solute concentration gradient in diffusiophoresis, the Joule heating effect in the applied electric field driven case (i.e., electrophoresis) is absent, and there is no particle-electrode contact. However, the mechanisms involved in diffusiophoresis can be more complicated than that in electrophoresis. For a charged particle in a salt solution, these include chemiphoresis, where particles are driven by an unbalanced ionic distribution and double layer polarization (DLP), and electrophoresis, where they are driven by a local electric field arising from the difference in ionic diffusivities. Due to DLP, the particle behavior is also influenced hydrodynamically by the flow of the ion-rich fluid inside (outside) the double layer towards the low (high) salt concentration direction (i.e., osmotic flow).

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Toroidal shaped entities are not uncommon in biological science. For instance, bacterial DNA, plasmid DNA of eukaryotic cells, and most viral DNA can all be isolated as a single intact toroidal chromosome. While free DNA in solution is of linear shape, the DNA in living cells is highly condensed into toroidal arrays, especially in sperm cells and viruses where gene transcription is inactive [13–15]. Kong [16] found that *Escherichia coli* has a toroidal structure with a hole large enough to encircle double-stranded DNA. Eickbush and Moudrianakis [17] suggested that the toroidal shape of the double-helix in DNA appearing in organisms relate to its charge density and the water activity of the immediate microenvironment. Anabaenopsis is another example of toroidal biocolloids.

Often, biocolloids such as DNAs, RNAs, and proteins are simulated by polyelectrolyte (PE), a porous, high molecular weight entity bearing dissociable functional groups, the dissociation of which in an aqueous medium yields fixed charge. Typical example for PE includes polyampholytes [18] and permuted PE [19]. The behavior of PEs in an applied field has been studied by many researches. For instance, Hsu et al. [20] modeled the diffusiophoresis of an isolated spherical PE. Tseng et al. [21] and Tseng et al. [22] discussed respectively the influence of the shape and the aspect ratio of a non-spherical PE on its mobility.

Although toroid electrophoresis has been studied previously (e.g., Hsu et al. [23]), its diffusiophoresis has not been modeled, so far. Considering the potential applications of PE diffusiophoresis in modern nanotechnology, extending relevant analyses of electrophoresis to this applied concentration gradient driven phenomenon is highly desirable and necessary. This is done in the present study.

2. Theory

As illustrated in Fig. 1, we consider the diffusiophoresis of an isolated, charged toroidal polyelectrolyte (PE) of inner radius $(h - a)$ and outer radius $(a + h)$ subject to an applied uniform salt concentration gradient ∇n_0. The PE bears fixed charge of density ρ_{PE}. The cylindrical coordinates r, θ, z are adopted with the origin at the PE center, and ∇n_0 is in the z direction. Ω_p denotes the PE surface. A cylindrical computation domain is adopted with boundaries Ω_c, Ω_i, and Ω_o.

Suppose that the liquid phase is an incompressible Newtonian fluid, and the system is at a pseudo-steady state. Then the electric potential, ϕ, the fluid velocity, $\mathbf{v}$, the flux of ionic species j, $\mathbf{N_j}$, and the pressure, p can be described by

$$\nabla^2 \phi = -\frac{\rho_e + i\rho_{PE}}{\varepsilon} = -\sum_{j=1}^{2} \frac{z_j e n_j}{\varepsilon} - \frac{i\rho_{PE}}{\varepsilon} \tag{1}$$

$$\nabla \cdot \mathbf{v} = 0 \tag{2}$$

$$\eta \nabla^2 \mathbf{v} - \nabla p - \rho \nabla \phi - i\gamma \mathbf{v} = \mathbf{0} \tag{3}$$

$$\mathbf{J}_j = n_j \mathbf{v}_j = n_j \mathbf{v} - D_j \left(\nabla n_j + \frac{z_j e n_j}{k_B T} \nabla \phi \right) \tag{4}$$

$$\nabla \cdot \mathbf{J}_j = 0, j = 1, 2, \ldots, N \tag{5}$$

∇ and ∇^2 are the gradient operator and Laplacian, respectively. ε, η, k_B, e, T and ρ_e are the liquid permittivity, its viscosity, Boltzmann constant, the elementary charge, temperature and the space charge density, respectively. n_0 and n_{0e} are the bulk and the equilibrium bulk salt concentrations, respectively. $\nabla^* = a\nabla$, $n_0^* = n_0/n_{0e}$, and $\gamma = \nabla^* n_0^*$ is the scaled applied salt gradient; z_j, n_j, and D_j are the valence, the number concentration, and the diffusivity of ionic species j, respectively. i is a region index, $i = 1$ (0) for the region inside (outside) the PE. For simplicity, we
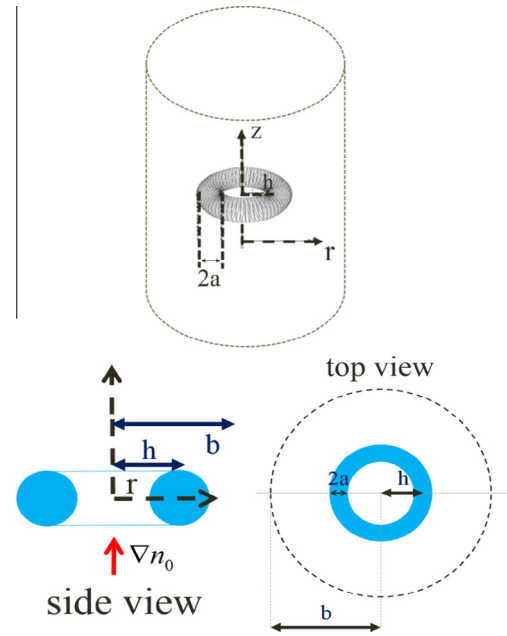

Fig. 1. Diffusiophoresis of a toroidal PE of inner radius $(h - a)$ and outer radius $(a + h)$ driven by an applied uniform salt concentration gradient ∇n_0; r, θ, and z are the radial, azimuthal, and axial axes of the cylindrical coordinates chosen with its origin at the PE center. Ω_p: PE surface; Ω_c, Ω_i, and Ω_o: boundaries of cylindrical computation domain.

assume that the ε and η of the liquid inside the PE are the same as those outside it.

Suppose that the values of ϕ, $\mathbf{v}$, and p at a point far away from the PE are uninfluenced by its presence. Then the following boundary conditions apply:

$$\mathbf{n} \cdot \nabla \phi = 0 \text{ on } \Omega_c \tag{6}$$

$$\phi = 0 \text{ on } \Omega_i \text{ and } \Omega_o \tag{7}$$

$$C = C_{high} \text{ on } \Omega_o \text{ on } \Omega_o \tag{8}$$

$$C = C_{low} \text{ on } \Omega_i \tag{9}$$

$$\mathbf{n} \cdot \mathbf{J}_j = 0 \text{ on } \Omega_c \tag{10}$$

We also assume that the fluid velocity, the hydrodynamic stress, the electric potential, and the electric field are all continuous on the PE-liquid interface.

The PE velocity U_p can be determined from that the sum of the forces acting on it vanishes at steady state. These forces include the electric force $\mathbf{F_E}$ and the hydrodynamic force $\mathbf{F_D}$. Letting F_E and F_D be the z components of $\mathbf{F_E}$ and $\mathbf{F_D}$, respectively, then $F_E + F_D = 0$, where [24,25]

$$F_E = \iint_{\Omega_p} (\boldsymbol{\sigma}^E \cdot \mathbf{n}) \cdot \mathbf{e}_z d\Omega_p \tag{11}$$

$$F_D = \iint_{\Omega_p} (\boldsymbol{\sigma}^D \cdot \mathbf{n}) \cdot \mathbf{e}_z d\Omega_p \tag{12}$$

$\boldsymbol{\sigma}^E$ and $\boldsymbol{\sigma}^D$ are the Maxwell stress tensor and the hydrodynamic stress tensor, respectively. For convenience, the present problem is partitioned into two sub-problems: in sub-problem 1, ∇n_0 is not applied and the toroid is moving with the constant velocity U_p, and in sub-problem 2, ∇n_0 is applied but the toroid is fixed. Let F_i, F_{Ei}, and F_{Di} be the z components of the total force, the scaled electric force, and the scaled hydrodynamic force acting on the toroid in sub-problem i, respectively. Then $F_1 = \chi_1 U_p$ and $F_2 = \chi_2 \nabla n_0$, where χ_1 and χ_2 are proportional constants, $U_p = -\frac{\chi_2}{\chi_1} \nabla n_0$. For convenience, dimensionless forces scaled by the