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The physics of the movement of a composite microparticle with a thin ion-selective shell in an external electric field

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The movement of a nonuniform particle in an electrolyte solution under the action of an external electric field is considered in the work. The inner part (the core) of the particle is assumed to be a solid dielectric, which is surrounded by a thin ion-selective shell. It is believed that such a model describes the behavior of a number of real particles (especially biological ones) more precisely than the uniform one. The features of electrophoretic movement of such a particle have been theoretically investigated, the velocity of this movement has been obtained, a comparison with electrophoresis of a uniform dielectric particle and of a uniform ion-selective particle has been made. Several movement regimes have been found, their stability has been estimated.

Keywords: electrophoresis, composite particle, electroosmosis, concentration polarization, instability.

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The phenomenon of electrophoresis, which is the motion of particles in a liquid under the influence of an external electric field, allows for efficient control of microparticles (in particular, in lab-on-chip (LOC) devices) in medical diagnostics and chemical analysis [1]. One of the key characteristics of such motion is the dependence of the microparticle's velocity on the intensity of an external electric field. Dielectric particles were the examined initially [2], and a linear dependence was obtained for them. Later Dukhin has demonstrated [3] that this dependence for ion-selective particles in strong fields becomes quadratic. A deviation from the linear dependence in the case of strong fields and highly charged particles has also been predicted in theoretical studies performed by Yariv's group [4]. The nonlinear nature of this dependence has later been confirmed experimentally [5].

Electrophoresis of ion-selective particles in a liquid electrolyte has a much more complex behavior due to the presence of concentration polarization and electrokinetics of the second kind [6,7]. The rate of electrophoresis remains linearly dependent on the field intensity as long as the latter is low [8]. This linearity is violated at higher field strengths [9], and various flow regimes with different types of instabilities arise in strong fields [10].

The shape and internal structure of a particle were neglected in the theoretical studies discussed above. This approach is ill-suited to the study of biological particles and cells [11,12]. The model of a composite particle consisting of several concentric layers fits more, while still preserving the simplicity of theoretical research. Theoretical studies focused on composite particles are relatively few in number [13,14] and are often limited to the case of a weak field that allows for linear approximation of motion. Direct numerical modeling is the only existing method capable to provide a complete description of the electrophoresis of composite particles. It was used to examine qualitatively the flow around a stationary microparticle in [15], and the aim of the present study is to investigate electrophoretic motion.

A spherical microparticle with radius r_0 consisting of a spherical dielectric core with surface charge density σ and a homogeneous ion-selective shell with thickness L is considered (Fig. 1). The particle is submerged into a dilute solution of a symmetric binary univalent electrolyte with salt concentration C_∞; the system is exposed to an external electric field with intensity E_∞.

If we neglect chemical reactions and dissociation of the solvent liquid, the behavior of this system may be described with the system of Nernst–Planck, Poisson, and Navier–Stokes equations in the Stokes approximation:

$$\frac{\partial C^\pm}{\partial t} + \mathbf{U}\cdot\nabla C^\pm = \frac{DF}{RT}\nabla\cdot\left(\pm C^\pm\nabla\Phi\right) + D\nabla^2 C^\pm, \quad (1)$$

$$\varepsilon\nabla^2\Phi = -F\left(C^+ - C^-\right), \quad (2)$$

$$\nabla\Pi - \mu\nabla^2\mathbf{U} = -F\left(C^+ - C^-\right)\nabla\Phi,\ \nabla\cdot\mathbf{U} = 0. \quad (3)$$

The unknown functions are molar concentrations of ions $C^\pm$, electric potential Φ, pressure Π, and velocity vector $\mathbf{U}$. Symbol F denotes the Faraday constant, R is the universal gas constant, T is absolute temperature, D is the ion diffusion coefficient, μ is the dynamic viscosity of the electrolyte solution, and ε is its absolute permittivity. The permittivity of the shell is also assumed to be equal to ε, and the core permittivity is denoted as ε_p.

The system of equations (1)–(3) is written in the spherical coordinate system with its origin at the particle's center. Therefore, the particle motion is represented as an oncoming flow of the electrolyte solution with velocity U_∞ (i.e., the

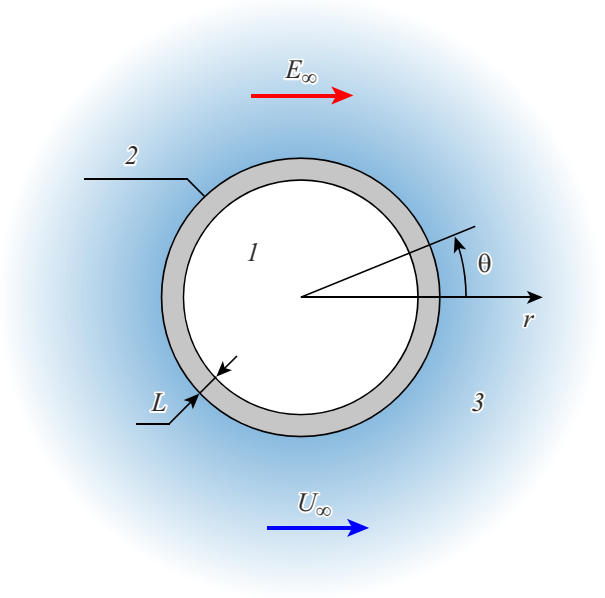

Figure 1. Schematic diagram of a composite microparticle. *1* — Dielectric solid core, *2* — ion-selective shell, and *3* — electrolyte solution.

particle moves in the direction opposite to the arrow in Fig. 1). The three-dimensional system of equations allows for an axisymmetric solution with the axis of symmetry passing through the particle's center and directed along the external electric field. With this simplification introduced, the only spatial variables remaining are the radius r and the polar angle $0 \leqslant \theta \leqslant \pi$.

The system (1)–(3) is valid in region $r > r_0$. Inside the core ($r < r_0 - L$), only Poisson equation (2), which degenerates into Laplace equation $\nabla^2\varphi = 0$, is applicable (for convenience of further analysis, the core's electric potential is denoted as φ). The shell is considered to be impermeable to liquid but permeable to ions, so $\mathbf{U} = 0$ should be assumed in Eq. (1). The following additional term arises in (2):

$$r_0 - L < r < r_0: \quad \varepsilon\nabla^2\Phi = -F\left(C^+ - C^- + N\right). \qquad (4)$$

The quantity N in (4) has the physical meaning of the space charge density and specifies the selectivity of the shell: it is cation- and anion-selective at $N < 0$ and $N > 0$, respectively. At $|N| \gg C_\infty$, the selectivity tends to the ideal one. This model has already been used by the authors in the study of flat non-ideal membranes [16].

The electric potential is assumed to be continuous throughout the entire space and has no singularity at the point $r = 0$. A jump in field strength is observed and the ion flow is absent at the boundary of the core:

$$r = r_0 - L: \quad \varepsilon\frac{\partial\Phi}{\partial r} = \varepsilon_p\frac{\partial\varphi}{\partial r} - \sigma,$$

$$\Phi = \varphi, \quad \pm\frac{F}{RT}C^\pm\frac{\partial\Phi}{\partial r} + \frac{\partial C^\pm}{\partial r} = 0. \qquad (5)$$

At the outer boundary of the shell ($r = r_0$), no-slip conditions are set for $\mathbf{U} = 0$; and the continuity conditions for Φ and $C^\pm$ are satisfied. Away from the particle, the ion concentrations tend to the equilibrium value, the field strength tends to that of the external field, and the velocity tends to that of the oncoming flow.

$$r \to \infty: \quad C^\pm \to C_\infty, \Phi \to -E_\infty r\cos\theta,$$

$$U_\theta \to -U_\infty\sin\theta, \quad U_r \to -U_\infty\cos\theta. \qquad (6)$$

The concentrations of electrolyte ions at the initial time ($t = 0$) are assumed to be equal to the equilibrium value, $C^\pm = C_\infty$.

The system (1)–(6) is solved numerically in the region $r_0 - L < r < R_{\max}$, where $R_{\max} \gg r_0$, using the grid method of the second order of approximation in space and the third one in time. The distribution of potential φ is determined analytically. The condition of balance between the viscous and electric forces acting on the particle is used to calculate U_∞. A detailed description of the numerical method was provided in [17].

It is natural to compare the behavior of a composite particle with that of similar dielectric [17] and ion-selective [9,10] ones. The velocity of the ion-selective particle in weak fields is given by the Helmholtz–Smoluchowski formula

$$U_\infty = \frac{\varepsilon\xi}{\mu}E_\infty, \qquad (7)$$

where ξ is the zeta potential calculated through σ. A similar relation for an ion-selective particle was proposed in [9]:

$$U_\infty = \frac{\varepsilon\xi}{\mu}\left(1 - 0.22\frac{\xi F}{RT}\right)E_\infty. \qquad (8)$$

These dependences change in strong fields: the approximation (7) is refined with an $O(E_\infty^3)$ term [18], and (8) is replaced either with a quadratic dependence $U_\infty \propto E_\infty^2$ [3] or a weaker one. $U_\infty \propto E_\infty^{4/3}$ [9].

The calculations were performed for particles with a radius of $5\,\mu$m and a $0.5\,\mu$m shell in an aqueous solution of potassium chloride with the concentration of 0.1 mol/m^3. The shell thickness is taken relatively small (10 %) to make the comparison of composite and dielectric particles valid. The value of N is assumed to be 10 times higher than the concentration of the solution $N = -1$ mol/m^3. The calculations show that the motion of the composite particle does not depend qualitatively on σ. Specifically, at a relatively strong field of 500 kV/m and σ varying from zero to a moderate level of $+55\,\mu$C/m^2, the value of U_∞ changes by 12 %. When σ varies in the opposite direction (to $-55\,\mu$C/m^2), the velocity changes just by 3 %. The dependence on σ is much more pronounced for the dielectric particle: as the charge varies from -55 to $-62\,\mu$C/m^2 (which is also a moderate value), the velocity changes by 15 %.

Figure 2 presents the dependences of the electrophoresis rate on the applied field intensity. The electrophoresis of

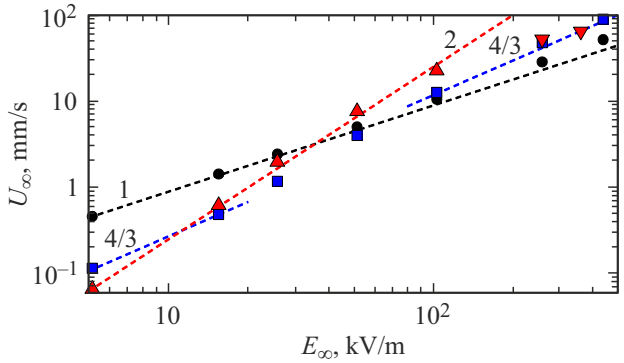

Figure 2. Comparison of electrophoresis rates of dielectric (circles), composite (squares), and ion-selective (triangles) particles. $\sigma = -55\,\mu$C/m^2. Downward-pointing triangles indicate the instability of the concentration jet. Dotted lines are the power asymptotics; the power-law exponent is indicated on the plot.

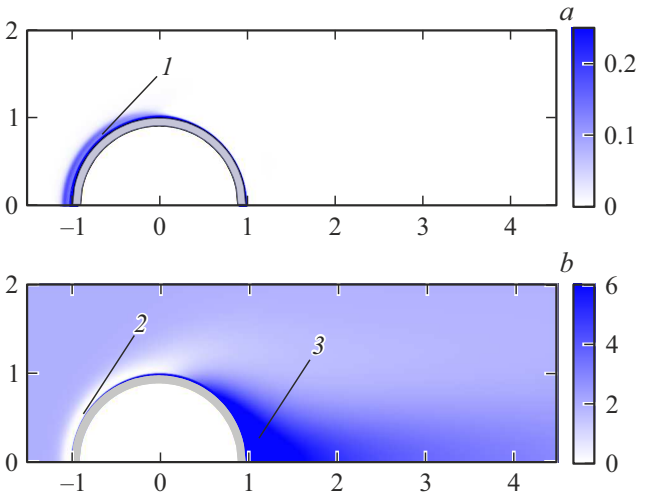

Figure 3. Normalized charge density ρ/C_∞ (a) and salt concentration K/C_∞ (b) near a composite particle. $E_\infty = 500$ kV/m; $\sigma = -62\,\mu$C/m^2. The unit of distance is r_0. *1* — Space charge region, *2* — depletion layer, and *3* — enriched region.

the first kind (7) is observed for the dielectric particle at $E_\infty < 100$ kV/m; a pronounced nonlinearity emerges at field strength above 300 kV/m. In the case of the ion-selective particle, the second-kind regime appears already at 5 kV/m. The dependence of the velocity on the field intensity is quadratic at first, but then gets weaker, to a power of 4/3. An electrokinetic instability emerges at an intensity of about 80 kV/m, leading to the formation of additional vortices near the particle's surface at its front [9]. These vortices are carried backwards along the surface and eventually vanish. At field strengths above 500 kV/m, the vortices are generated so actively that the behavior of the electrolyte solution near the particle appears chaotic.

The second-kind regime is also established for the composite particle, but the electrokinetic instability is observed much later, at $E_\infty > 600$ kV/m. The velocity of the composite particle at low and high E_∞ follows closely the $U_\infty \propto E_\infty^{4/3}$ law (for clarity, the corresponding asymptotics are drawn separately); at moderate E_∞, the power exponent reaches 5/3.

The distributions of salt $K = C^+ + C^-$ and charge density $\rho = C^+ - C^-$ are shown in Fig. 3. In sufficiently strong fields, a space charge region is formed in front of the particle, and a concentration jet is formed behind it. This behavior is typical of both ion-selective and dielectric particles. The jet behind the ion-selective particle becomes unstable at a field strength about of 200 kV/m: the boundary of region *3* in Fig. 3, *b* starts to oscillate [10]. The particle's velocity also oscillates, and Fig. 2 shows its time-averaged values in this regime. The jet behind the composite particle remains stable within a wider range of field intensities (up to $E_\infty \sim 500$ kV/m), which is closer to the behavior of dielectric particles. Although the shell is rather thin, concentration polarization is observed near the composite particle, which is typical of the ion-selective particle.

A theoretical study of electrophoresis of a two-layer particle with a thin shell was carried out. Its velocity was calculated. It turned out to be similar to the velocity of an ion-selective particle and virtually independent of the core charge. Concentration polarization and electrokinetic instability were detected near the composite particle; in addition, the concentration jet behind the particle was found to be unstable. Compared to the ion-selective particle, these instabilities emerge at significantly higher electric field intensities.

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Conflict of interest

The authors declare that they have no conflict of interest.

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