

Electrophoretic Motion of a Liquid Droplet within an Uncharged Cylindrical Pore

Cheng-Hsuan Huang, Eric Lee

Abstract—Electrophoretic motion of a liquid droplet within an uncharged cylindrical pore is investigated theoretically in this study. It is found that the boundary effect in terms of the reduction of droplet mobility (droplet velocity per unit strength of the applied electric field) is very significant when the double layer surrounding the droplet is thick, and diminishes as it gets very thin. Moreover, the viscosity ratio of the ambient fluid to the internal one, σ , is a crucial factor in determining its electrophoretic behavior. The boundary effect is less significant as the viscosity ratio gets high. Up to 70% mobility reduction is observed when this ratio is low ($\sigma = 0.01$), whereas only 40% reduction when it is high ($\sigma = 100$). The results of this study can be utilized in various fields of biotechnology, such as a biosensor or a lab-on-a-chip device.

Keywords—Cylindrical pore, Electrophoresis, Lab-on-a-chip, Liquid droplet

I. INTRODUCTION

MICRO-/NANOFLUIDICS is a rapidly developing technology that involves fluid handling in devices containing channels in the micro-/nanometer size regime. This miniaturization offers many advantages including the ability to handle nanoliters of fluid and to provide fast response times [1-3]. In the past decade, with the fast development of micro- and nanotechnology, research can be performed in very controllable and direct ways. Ideally, micro-/nano- technology can realize each process, such as sampling, sample pretreatment, reaction, separation, detection and analysis in an analytical system on one integrated microdevice. Integrated systems of micro-/nanofluidic channels combined with pumps, valves, and detectors are known as Micro-total-analysis-system (μ TAS) [4] or Lab-on-a-Chip (LOC) [5].

Generally, the fluids of interest in chemistry and biotechnology are rarely simple single-phase liquids. Complex fluidic systems, such as emulsions, play a very important role in drug delivery, food science, oil and dairy industries, and therefore require detailed study. When different phases are injected as adjacent streams in one channel, one phase often preferentially wets the boundaries and encapsulates the second fluid as discrete droplets due to the high interfacial forces on microscales [6]. Droplet-based multiphase flow offer controlled mini-volumes of droplets. These tiny droplets are

almost ideal chemical reactors characterized by fast thermal transfer, efficient mixing, narrow residence time and an absence of hydrodynamic dispersion. These flows have been therefore utilized in emulsification and encapsulation [7], synthesis [8], mixing [9], and bioassay [10], and so forth. Furthermore, in a droplet-based multiphase flow, droplets are separated from channel walls by a thin layer of another immiscible (carrier) fluid, therefore the internal compositions in droplets can not disperse across the boundary and can be cleanly transported without contacting the channel walls [11]. This supplies us with more flexibility to apply each droplet as a separate microreactor.

Flow in micro-/nanochannels can be driven not only by external pressure or internal forces, but also by an electrical, magnetic, thermal, photic or phonic field. The movement of a charged particle relative to the surrounding fluid as a response to the applied electric field, for example, is termed electrophoresis, which has great potentials in analytical chemistry and a separation method in industrial processes [12]. As for the electrophoresis of droplets in particular, Booth [13] first investigated the electrophoretic behavior of a mercury drop. Later on, Levine and O'Brien [14] examined thoroughly the motion of a mercury drop and found that it can be influenced significantly by an externally applied static electric field. Baygents and Saville [15]-[16] analyzed the electrophoretic mobility as a function of the zeta potential for conducting and non-conducting drops. Ohshima [17] extended the study to concentrated dispersion of charged spherical mercury drops and derived a formula for it. It is found that if the surface potential of a mercury drop is sufficiently high its electrophoretic behavior is the same as that of the corresponding rigid particle, the so-called solidification phenomenon of a liquid entity. Recently, Lee et al. [18] analyzed the electrophoresis of a non-rigid particle in a spherical cavity, and later extended to the case where the surface of a drop is of charge-regulated nature, a more general condition which arises from the dissociation of functional groups [19]. In general, because the particle-dispersion medium interface is not non-slip, the electrophoretic mobility of a non-rigid particle is larger than that of the corresponding rigid particle.

Meanwhile, the presence of a boundary plays a key role in many applications of electrophoresis as well. In the field of corresponding theoretical analysis of a charged rigid particle in a cylindrical channel, Keh and Anderson [20] studied the electrophoresis of a charged rigid particle within an uncharged wall under the assumption of very thin double layer. Anderson and Ennis [21] studied the effect of finite double layer

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Cheng-Hsuan Huang is with the Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan.

*Correspondence: Professor Eric Lee, Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan. (Tel: 886-2-23622530; Fax: 886-2-23622530; e-mail: ericlee@ntu.edu.tw)

thickness, but the zeta potential had to be low to make possible the theoretical treatment there. Shugai and Carnie [22] investigated the problem again with the numerical method proposed by Teubner [23]. No restriction of double layer thickness was imposed. Moreover, the double layer of the particle was allowed to touch the cylindrical boundary. Later, Hsu et al. [24] considered the electrophoresis of a soft particle and a charge-regulated soft particle respectively along the centerline of a cylindrical pore, assume low surface potential at the inner hard core. They found that an uncharged wall would retard the particle motion as a result of the viscous drag.

The presence of surfactant or surface-active substances may lead to a significant impact on the motion of a liquid droplet. Usually, a tiny surfactant concentration, which is always present in tap water, natural water, and electrolyte samples, affects the rheology of fluid interfaces, for example, the surface viscosity and the surface tension. However, the incorporation of a general consideration of surfactant effect proves to be a formidable task for the current study. In the case of ultrapure water and ultrapure salts, the droplet surface is mobile, and the so-called Rybczynski-Hadamard theory [25] in hydrodynamics is applicable in this study.

In this study, the electrophoretic motion of a liquid droplet within an uncharged cylindrical pore is considered. The external electric field is applied along the axis of the pore and the droplet is positioned on the centerline so that the droplet moves along the axis of the cylindrical pore. We focus on the impact on the droplet mobility due to the presence of the cylindrical pore. Parameters of electrokinetic interest are examined, such as the double layer thickness of the droplet, the relative magnitude of the viscosity of the droplet and that of the surrounding fluid, the ratio of pore-to-droplet radii, and so on. A pseudo-spectral method [26] based on Chebyshev polynomials is used to solve the resulting general electrokinetic equations numerically. This method has proven to be very powerful in solving various electrokinetic systems of interest. This study provides important fundamental information about the electrophoretic behavior of liquid droplet in micro- or nano-channels, which is essential to the successful design and operation of microreactor or LOC devices, used frequently in biochemical or biological fields. The conventional technique of capillary electrophoresis (CE) is also closely related to the system studied here, thus may benefit from it as well.

II. THEORY

The system under study here is illustrated in Fig. 1, where a spherical droplet of radius a moves with velocity \mathbf{U} along the axis of a cylindrical pore of radius R_b in response to an applied uniform electric field \mathbf{E} in the Z -direction. The cylindrical pore is filled with an aqueous solution containing $z_1 : z_2$ electrolytes, where z_1 and z_2 are the valences of cations and anions. The electroneutrality in the bulk liquid phase requires that $n_{20} = n_{10}/\alpha$, where n_{10} and n_{20} being respectively the bulk concentrations of cations and anions and $\alpha = -z_2/z_1$. Spherical coordinates (r, θ, φ) is adopted to describe the internal liquid phase, and the cylindrical coordinates (R, Θ, Z) is applied to region external to the droplet as well as the cylindrical wall.

The origin of the spherical coordinate is located at the center of the liquid droplet and the symmetric nature of the problem suggests that only half of the (r, θ) domain needs to be considered.

The main assumptions in our analysis are as follows. (i) The Reynolds number of the liquid flow is small enough to ignore inertial terms in the Navier–Stokes equations and the liquid can be regarded as incompressible. (ii) The applied field \mathbf{E} is weak so that the liquid droplet velocity \mathbf{U} is proportional to \mathbf{E} and terms of higher order in \mathbf{E} may be neglected. In practice this means \mathbf{E} is small compared with the fields that occur in the double layer, with $|\mathbf{E}| \ll \zeta\kappa$, the characteristic electric field measured by the zeta potential divided by the double layer thickness. (iii) The permittivity ε takes the same value both inside and outside the liquid droplet. (iv) The droplet surface is considered mobile, and the so-called Rybczynski-Hadamard theory, which assumes both the velocity and the shear stress are continuous across the droplet surface in hydrodynamics is employed. The governing equations for the problem here are, respectively, the Poisson equation, the Stokes equation inside the liquid droplet ($0 < r < a$) and outside the liquid droplet with an extra consideration of the electric force ($r > a$). To simplify the treatment, subsequent discussions are based on scaled symbols, i.e., the governing equations are rewritten in dimensionless form. The following symbols are chosen for the characteristic variables: the radius of liquid droplet, a , the thermal electric potential per valence of cations, ϕ_0 (defined as $k_B T / z_1 e$), the bulk concentration of the cations, n_{10} , and the velocity based on Smoluchowski's theory [27] when an external electric field ϕ_0/a is applied, $U_E = \varepsilon \phi_0^2 / \mu_0 a$. Corresponding dimensionless variables are listed as follows: $r^* = r/a$, $R^* = R/a$, $Z^* = Z/a$, $n_j^* = n_j/n_{10}$, $\mathbf{E}^* = \mathbf{E}/(\phi_0/a)$, $\phi_e^* = \phi_e/\phi_0$, $\delta\phi^* = \delta\phi/\phi_0$, $\psi^* = \psi/U_E a^2$, $\zeta_a^* = \zeta_a/\phi_0$, $\mathbf{v}^* = \mathbf{v}/U_E$, $\kappa^{-1} = \sqrt{\varepsilon k_B T / \sum_{j=1}^2 n_{j0} (ez_j)^2}$, $\sigma = \mu_0/\mu_i$. The dimensionless forms

of the governing equations are with assuming low surface potential:

$$\nabla^{*2} \phi_e^* - (\kappa a)^2 \phi_e^* = 0, \quad (1)$$

$$\nabla^{*2} \delta\phi^* = 0, \quad (2)$$

$$E^{*4} \psi^* = 0, \quad 0 < r^* < 1, \quad (3)$$

$$E^{*4} \psi^* = -(\kappa a)^2 \left(\frac{\partial \phi_e^*}{\partial \theta} \frac{\partial \delta\phi^*}{\partial r^*} - \frac{\partial \phi_e^*}{\partial r^*} \frac{\partial \delta\phi^*}{\partial \theta} \right) \sin \theta, \quad r^* > 1. \quad (4)$$

At the center of the droplet, axial symmetry condition applies to both ϕ_e^* and $\delta\phi^*$. The cylindrical wall ($R^* = R_b^* = R_b/a$) is supposed to be nonconductive and uncharged. At the droplet–liquid interface, the boundary conditions such as the electric field, as well as the flow field on the surface of the droplet ($r^* = 1$) should be continuous. The zeta potential of droplet is assumed to be ζ_a^* . For convenience, we assume that the fluid is fixed, and the cylindrical pore moves with velocity $-U \mathbf{i}_z$, where \mathbf{i}_z is the unit vector along the axis. In addition, all variables must satisfy the axial symmetry condition as well at $\theta = 0, \pi$. To avoid divergence problem in calculation, the

boundary conditions of equilibrium potential and flow field in the Z -direction far away from the particle needs special treatment, as reported by Carnie [22]. We adopt an alternative approach here by assuming fully-developed flow and uniform electric potential distribution at both ends of a finite cylinder of length L . Hence at both ends the equilibrium potential can be adopted as $\partial\phi_e^*/\partial Z = 0$, and the velocity conditions can be taken as $\partial\psi^*/\partial Z = 0$ due to an uncharged pore. Instead, a finite value of L/a is selected, with one dimensional electric potential profile applied at both inlet ($Z^* = -L/a$) and outlet ($Z^* = L/a$). Based on these assumptions, the boundary conditions associated with the present problem are as follows:

$$\frac{\partial\phi_e^*}{\partial r^*} = 0, \quad r^* = 0, \quad (5)$$

$$\phi_e^* = \zeta_a^*, \quad r^* = 1, \quad (6)$$

$$\phi_e^* = 0, \quad R^* = \frac{R_b}{a}, \quad (7)$$

$$\frac{\partial\phi_e^*}{\partial Z^*} = 0, \quad Z^* = \pm \frac{L}{a}, \quad (8)$$

$$\frac{\partial\delta\phi^*}{\partial r^*} = 0, \quad r^* = 0, \quad (9)$$

$$\left. \frac{\partial\delta\phi^*}{\partial r^*} \right|_{r^*=1^-} = \left. \frac{\partial\delta\phi^*}{\partial r^*} \right|_{r^*=1^+}, \quad r^* = 1, \quad (10)$$

$$\frac{\partial\delta\phi^*}{\partial R^*} = 0, \quad R^* = \frac{R_b}{a}, \quad (11)$$

$$\frac{\partial\delta\phi^*}{\partial Z^*} = -E_z^*, \quad Z^* = \pm \frac{L}{a}, \quad (12)$$

$$\psi^* = 0 \quad \text{and} \quad \frac{\partial\psi^*}{\partial r^*} = 0, \quad r^* = 0, \quad (13)$$

$$\psi^* \Big|_{r^*=1^-} = \psi^* \Big|_{r^*=1^+}, \quad \frac{\partial\psi^*}{\partial r^*} \Big|_{r^*=1^-} = \frac{\partial\psi^*}{\partial r^*} \Big|_{r^*=1^+} \quad \text{and}$$

$$\left(\frac{\partial^2\psi^*}{\partial r^{*2}} - \frac{2}{r^*} \frac{\partial\psi^*}{\partial r^*} \right) \Big|_{r^*=1^-} = \left(\frac{\partial^2\psi^*}{\partial r^{*2}} - \frac{2}{r^*} \frac{\partial\psi^*}{\partial r^*} \right) \Big|_{r^*=1^+}, \quad r^* = 1, \quad (14)$$

$$= \sigma \left(\frac{\partial^2\psi^*}{\partial r^{*2}} - \frac{2}{r^*} \frac{\partial\psi^*}{\partial r^*} \right) \Big|_{r^*=1^+}, \quad r^* = 1,$$

$$\psi^* = \frac{1}{2} U^* R^{*2}, \quad \text{and} \quad \frac{\partial\psi^*}{\partial R^*} = U^* R^*, \quad R^* = \frac{R_b}{a}, \quad (15)$$

$$\psi^* = \frac{1}{2} U^* R^{*2}, \quad \text{and} \quad \frac{\partial\psi^*}{\partial Z^*} = 0, \quad Z^* = \pm \frac{L}{a}. \quad (16)$$

$$\frac{\partial\phi_e^*}{\partial\theta} = \frac{\partial\delta\phi^*}{\partial\theta} = \frac{\partial\psi^*}{\partial\theta} = \psi^* = 0, \quad \theta = 0, \pi. \quad (17)$$

According to O'Brien and White [28], the present problem can be divided into two sub-problems. In the first problem, the droplet moves in the absence of the applied electric field, \mathbf{E} , and in the second problem \mathbf{E} is applied, but the droplet is kept fixed instead. In the first problem the total force acting on a droplet in the vertical direction, F_1 , is proportional to its electrophoretic

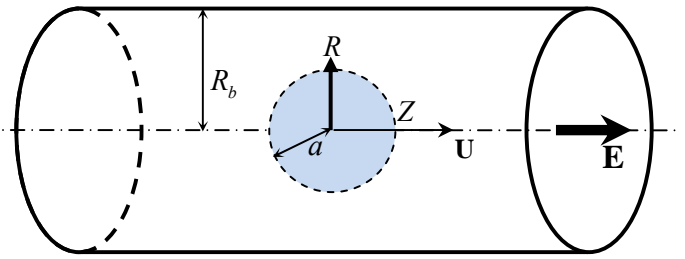


Fig. 1 Schematic representation of the problem considered where a liquid droplet of radius a is placed on the axis of a long cylindrical pore of radius R_b . A uniform electric field \mathbf{E} parallel to the axis of the pore is applied in the Z -direction.

velocity, U^* , while in the second problem the total force, F_2 , is proportional to the applied electric field, E_z^* . Therefore, we have $F_1 = c_1 U^*$ and $F_2 = c_2 E_z^*$. Because $F_1 + F_2 = 0$ at steady state, the dimensionless electrophoretic mobility, μ_m^* , can be expressed as

$$\mu_m^* = \frac{U^*}{E^*} = -\frac{c_2}{c_1}. \quad (18)$$

Note that both c_1 and c_2 are independent of U^* and E^* . The forces acting on a droplet F_i comprises the electric force F_{iEz} and the hydrodynamic force F_{iDz} , where the subscript i represents sub-problem 1 and 2. Once F_{iEz} and F_{iDz} are evaluate, c_i and μ_m^* can be obtained easily.

III. RESULTS AND DISCUSSION

Key parameters are examined for their respective influence on the system under consideration, that is, the electrophoretic behavior of a charged liquid droplet along the axis of an uncharged cylindrical pore. We assume that the pore is sufficiently long so that the end effects of the flow field can be neglected. To make sure that this is appropriate, the scaled transition length of a pore L , the shortest length to achieve fully developed flow, is tested under conditions of interest. It turns out that a length L equivalent to roughly six times that of the droplet radius is sufficient to assume a fully developed flow field.

Fig. 2 illustrates the variation of the droplet mobility as a function of the scaled double layer thickness κa at various viscosity ratios σ (μ_o/μ_i). Here, a large value of σ (say, $\sigma = 100$) simulates the case when gas bubbles are dispersed in a liquid phase. On the other hand, a small value of σ (say, $\sigma = 0$) simulates the case where rigid particles are dispersed in a liquid phase. Fig. 2 suggests that, for a fixed κa , the larger the value of σ , the greater the mobility of a droplet. This is mainly because of the fact that the shear drag force experienced by a nonrigid particle (such as bubble and liquid droplet) is smaller than that of a rigid particle. Fig. 2 also indicates that the larger the κa , the greater the difference between the mobilities of droplets of different viscosities.

The variations of the mobility μ_m^* as a function of the viscosity ratio σ at various double layer thickness κa are presented in Fig. 3. This figure reveals that if the double layer is

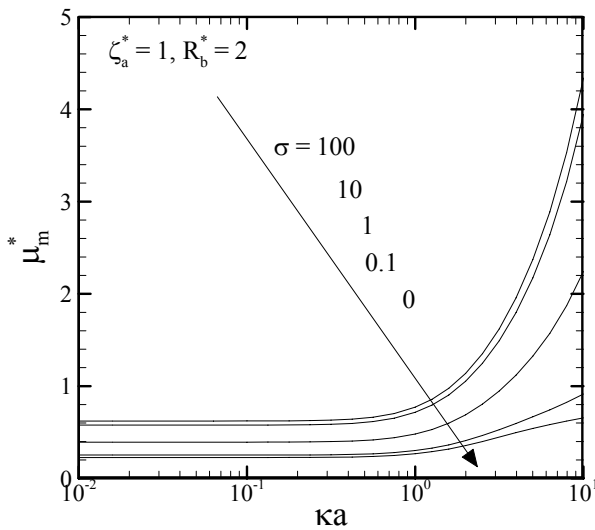


Fig. 2 Droplet mobility as a function of κa at different values of σ with $\zeta_a^* = 1, R_b^* = 2$

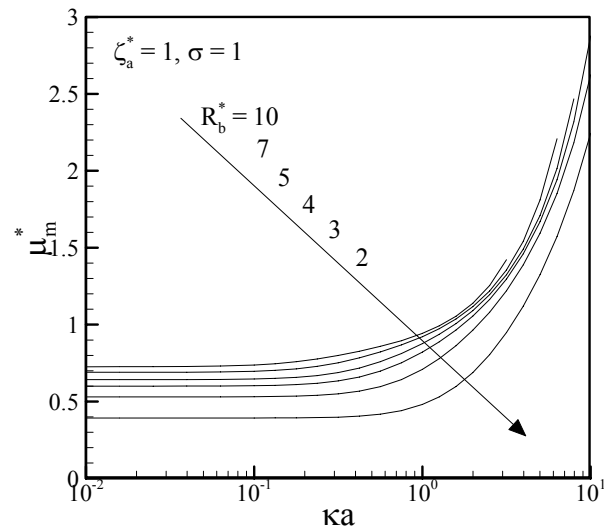


Fig. 4 Droplet mobility as a function of κa at different values of R_b^* with $\zeta_a^* = 1, \zeta_w^* = 0, \sigma = 1$

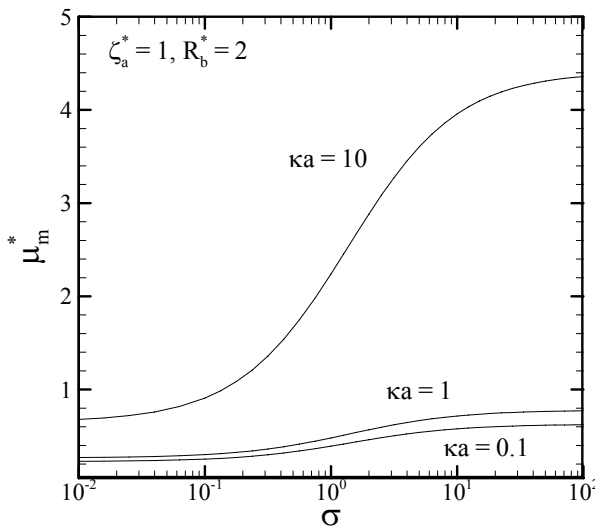


Fig. 3 Droplet mobility as a function of σ at different values of κa with $\zeta_a^* = 1, R_b^* = 2$

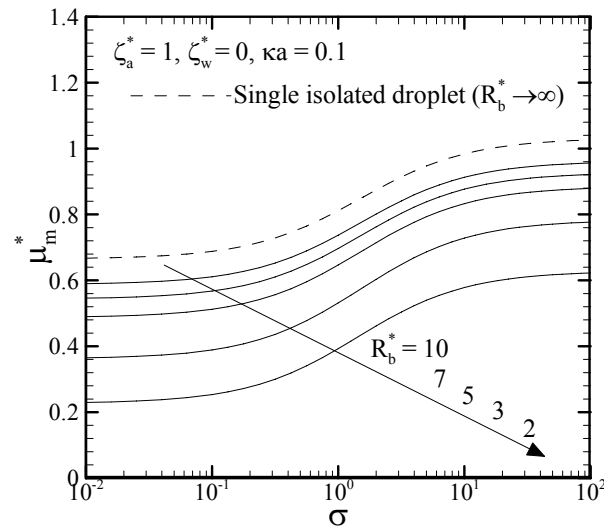


Fig. 5 Droplet mobility as a function of σ at different values of R_b^* with $\zeta_a^* = 1, \zeta_w^* = 0, \kappa a = 0.1$. The dashed-dot line represents the Ohshima's results [17] with the corresponding case of an isolated droplet

thick or medium, μ_m^* ($\sigma = 100$) is nearly 2-3 times of μ_m^* ($\sigma = 0.01$). For a thin double layer, however, μ_m^* ($\sigma = 100$) is up to 7-8 times of μ_m^* ($\sigma = 0.01$).

The boundary effect arising from the presence of the cylindrical pore, measured by the ratio of pore-to-droplet radii, R_b^* , on the droplet's electrophoretic mobility, μ_m^* , is presented in Fig. 4. The presence of the cylindrical pore "squeezes" the double layer surrounding the droplet when it is thick hence affects the droplet motion by means of both the electrostatic interaction and the hydrodynamic drag. As a result, the boundary effect, in terms of the reduction of droplet mobility, is most significant at small κa , whereas tends to diminish as κa increases, as shown in Fig. 4. The larger the radius of the cylindrical pore, the higher the droplet mobility. In Fig. 5, the variations of the mobility μ_m^* as a function of the viscosity ratio σ at various R_b^* is further considered. The larger the radius of the cylindrical pore, the larger the droplet mobility is, as expected. Moreover, the narrower the cylindrical

pore (R_b^*), the more significant the deviation of droplet mobility between different σ is. Compared with an isolated droplet in an infinite medium of electrolyte solution, for example, the boundary effect here for $R_b^* = 2$ amounts to a reduction of droplet mobility roughly by 40% for high σ ($\sigma = 100$) to around 70% for relatively low σ ($\sigma = 0.01$). In other words, the boundary effect is less significant as the viscosity ratio gets high due to the less hydrodynamic drag interaction between the cylindrical pore and the particle. The reduction in droplet mobility serves as a good measurement of the boundary effect.

IV. CONCLUSION

Electrophoresis of a charged liquid droplet along the centerline of an uncharged cylindrical pore is investigated theoretically in this study. A pseudo-spectral method based on

Chebyshev polynomial is used to solve the resulted general electrokinetic equations, and various key parameters are examined for their effects on particle motion. We find:

(a) The mobility of a droplet is greater than that of a rigid particle. This is because the shear drag force experienced by a nonrigid particle (such as bubble and liquid droplet) is smaller than that of a rigid particle. The larger the κa , the greater the difference between the mobilities of droplets corresponding to different viscosities.

(b) The boundary effect is very significant when double layer is thick and diminishes as it gets very thin, due to the profound electrostatic and hydrodynamic interaction associated with the severe physical deformation of double layer with a nearby cylindrical pore. Up to 70% reduction is observed when the viscosity ratio of the droplet is low.

The results of this study have potential applications in various microfluidic and nanofluidic operations, such as biosensors and lab-on-a-chip devices.

APPENDIX

Notations

a	the radius of the liquid droplet (m).
e	elementary electric charge (1.6×10^{-19} coul).
E	the applied field (volt/m).
E_z	the applied field in Z-direction (volt/m).
k_B	Boltzmann's constant (1.38×10^{-23} joule/K).
n_j	number concentration of the j_{th} ionic species ($\#/m^3$).
n_{j0}	bulk concentration of the j_{th} ionic species ($\#/m^3$).
p	pressure (Nt/m^2).
R	R-coordinate in the cylindrical coordinates.
R_b	the radius of the cylindrical pore (m).
r	r-coordinate in the spherical coordinates.
T	absolute temperature (K).
U	electrophoretic velocity of the particle (m/s).
U_E	the characteristic velocity based on Smoluchowski's theory (m/s).
v	fluid velocity (m/s).
v_s	the average velocity of electroosmotic flow (m/s).
Z	Z-coordinate in the cylindrical coordinates.
z_j	valence of the j_{th} ionic species.

Greek letters

α	valence ratio between negative and positive charged electrolytes.
ϵ	dielectric constant (coul/volt-m).
ζ_w	zeta-potential on the cylindrical wall (volt).
Θ	Θ -coordinate in the cylindrical coordinates.
θ	θ -coordinate in the spherical coordinates.
κ	reciprocal of the Debye length (1/m).
μ	viscosity of the fluid (Pa-s).
μ_i	viscosity of the internal fluid (Pa-s).
μ_o	viscosity of the surrounding fluid (Pa-s).
μ_m	electrophoretic mobility.
ρ	space charge density (coul/ m^3).

ϕ	ϕ -coordinate in the spherical coordinates.
ϕ	electric potential (volt).
σ	viscosity of the surrounding fluid/viscosity of the internal fluid.
ψ	stream function (m^3/s).

Superscripts

* dimensionless form.

Subscripts

e	equilibrium state.
0	macroscopic state.
1	cation.
2	anion.

Mathematical Operations

∇	the gradient operator.
∇^2	the Laplacian operator.

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