Langmuir

Subscriber access provided by NATIONAL TAIWAN UNIV

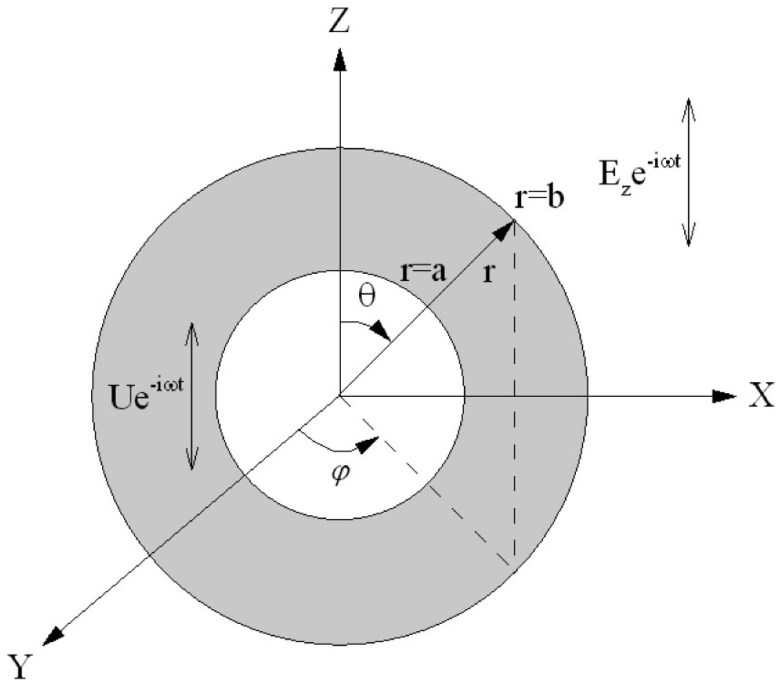
Research Article

Dynamic Electrophoresis of a Droplet in a Spherical Cavity

Eric Lee, Wei-Lun Min, and Jyh-Ping Hsu

Langmuir, **2006**, 22 (8), 3920-3928 • DOI: 10.1021/la0533821

Downloaded from http://pubs.acs.org on November 21, 2008



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

ACS Publications
High quality. High impact.

Langmuir is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Dynamic Electrophoresis of a Droplet in a Spherical Cavity

Eric Lee, Wei-Lun Min, and Jyh-Ping Hsu*

Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan 10617

Received December 14, 2005. In Final Form: February 16, 2006

The electrophoretic behavior of a droplet in a spherical cavity subject to an alternating electric field is analyzed theoretically under the conditions of an arbitrary level of surface potential and double-layer thickness. The influences of the thickness of the double layer, the level of surface potential, the size of a droplet, the viscosity of the droplet fluid, and the frequency of the applied electric field on the electrophoretic behavior of a droplet are examined through numerical simulations. We show that, because of the effect of double-layer deformation, the magnitude of the electrophoretic mobility of a droplet could have a local maximum and the phase angle could have a negative (phase lead) local minimum as the frequency of the applied electric field varies. In general, the lower the surface potential, the thicker the double layer and the larger the viscosity of the droplet fluid, and the more significant the boundary effect, the smaller the magnitude of the electrophoretic mobility of a droplet.

Introduction

Electroacoustic phenomena involve two basic effects: the colloid vibration potential and the electrokinetic sonic amplitude.[1] The former is a macroscopically measurable potential difference when a supersonic wave is applied to a colloidal dispersion. The latter is the reverse effect of the former, that is, the application of an alternating electric field to a colloidal dispersion yields a measurable supersonic wave. Several attempts have been made to model the electroacoustic phenomena. O'Brien,[2] for example, considered the dynamic electrophoresis of a spherical dispersion for the case of a thin double layer. The governing equations were solved numerically, and the results were used to evaluate the dynamic electrophoretic mobility. Sawatzky and Babchin[3] derived an approximate expression for the dynamic electrophoretic mobility of a spherical dispersion. Applying the numerical method of O'Brien, Magelsdorf and White[4] solved the electroacoustic equations for a spherical dispersion at low surface potential. Under the conditions of low surface potential and arbitrary double-layer thickness, Ohshima[5] derived an analytical expression for the dynamic mobility of a spherical dispersion. All these studies focused on the electrophoresis of rigid entities. For the case of nonrigid entities such as droplets, since the electric and the flow fields inside an entity may also need to be considered, solving the governing equations is usually more difficult than solving the corresponding equations for rigid entities.[6] Nonrigid dispersion is one of basic categories of colloidal dispersion, and is of practical significance in modern technology. Microemulsion systems, for instance, are often adopted to produce nanosized particles. Compared with the results for the electrophoresis of rigid entities, those for nonrigid entities are very limited.[6−13]

In practice, electrophoresis is often conducted in a confined space where boundary effect can play a significant role. A typical example includes electrophoresis in a porous medium where the influence of the porosity of a medium is usually not negligible. Capillary electrophoresis is another example where the presence of a capillary wall should be considered. Although the boundary effect on electrophoresis has been studied by many authors for the case in which a static electric field is applied, relevant analyses on cases in which a dynamic electric field is applied are very limited, especially when an entity is of a nonrigid nature. In this study, the boundary effect on the dynamic electrophoresis of a nonrigid entity is investigated by considering a droplet in a spherical cavity. A pseudospectral method based on Chebyshev polynomials is adopted to solve the governing electroacoustic equations and the associated boundary conditions. The influences of the key parameters of the system under consideration on the electrophoretic behavior of a droplet are examined. These include the frequency of the applied electric field, the thickness of the double layer surrounding a droplet, the relative size of a cavity, and the physical properties of a droplet, such as its surface potential and viscosity.

Theory

Referring to Figure 1, we consider the case where an electrolyte-free, Newtonian droplet of radius a is located at the center of a spherical cavity of radius b. Let $H = (a/b)^3$. An alternating electric field $E_z e^{-i\omega t}\mathbf{e}_z$ is applied along the z-axis, where t is time, E_z and ω are respectively the strength of the field and the frequency of the applied electric field, $\mathbf{e}_z$ is the unit vector in the z-direction, and $i = \sqrt{-1}$. Let $U e^{-i\omega t}\mathbf{e}_z$ be the electrophoretic velocity of the droplet. The spherical coordinates (r,θ,φ) are adopted, with its origin located at the center of the droplet. We consider the case where the liquid phase in the cavity is a Newtonian fluid containing z_1/z_2 electrolyte, with z_1 and z_2 respectively being the valences of cations and anions with $z_2 = -\alpha z_1$. For convenience, U is expressed as $U = U_R + iU_I$, in which U_R and U_I are respectively the real and imaginary parts of U. We assume that the strength of the applied electric field is relatively weak compared with that

---

* To whom correspondence should be addressed. Tel: 886-2-23637448. Fax: 886-2-23623040. E-mail: jphsu@ntu.edu.tw.

(1) Hunter, R. *J. Colloids Surf., A* **1998**, *141*, 37.
(2) O'Brien, R. W. *J. Fluid Mech.* **1988**, *190*, 71.
(3) Sawatzky, R. P.; Babchin, A. J. *J. Fluid Mech.* **1993**, *246*, 321.
(4) Mangelsdorf, C. S.; White, L. R. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 3567.
(5) Ohshima, H. *J. Colloid Interface Sci.* **1996**, *179*, 431.
(6) Baygents, J. C.; Saville, D. A. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 1883.
(7) Booth, F. *J. Chem. Phys.* **1951**, *19*, 1331.
(8) Levich, V. G. *Physicochemical Hydrodynamics*; Prentice Hall: Englewood Cliffs, NJ, 1962.
(9) Levine, S.; O'Brien, R. N. *J. Colloid Interface Sci.* **1973**, *43*, 616.
(10) Levine, S. *Materials Proceeding in the Reduced Gravity Environment of Space*; Rindone, G. E., Ed.; North-Holland: Amsterdam, 1981; Vol. 9, p 241.
(11) Ohshima, H.; Healy, T. W.; White, L. R. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 1643.
(12) Lee, E.; Kao, J. D.; Hsu, J. P. *J. Phys. Chem. B* **2002**, *106*, 8790.
(13) Lee, E.; Fu, C. H.; Hsu, J. P. *Langmuir* **2003**, *19*, 3035.

10.1021/la0533821 CCC: $33.50 © 2006 American Chemical Society
Published on Web 03/16/2006

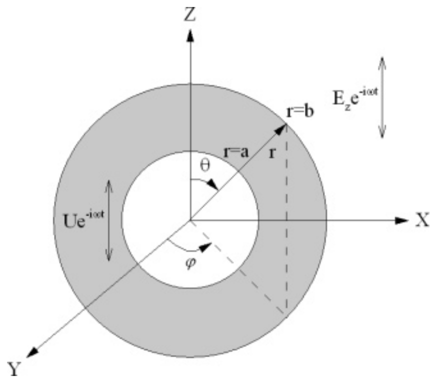


Figure 1. Illustration of the problem considered in which an electrolyte-free, Newtonian droplet of radius a is located at the center of a spherical cavity of radius b. An alternating electric field $E_z e^{-i\omega t}\mathbf{e}_z$ is applied along the z-axis and $Ue^{-i\omega t}\mathbf{e}_z$ is the electrophoretic velocity of the droplet. The spherical coordinates (r,θ,φ) are adopted with its origin at the center of droplet.

established by the droplet. The latter is on the order of surface potential/Debye length. Because the surface potential ranges from 25 to 150 mV and the Debye length ranges from 10 to 100 nm, the strength of the electric field established by the droplet is on the order of 2500 kV/m. In practice, the strength of the applied electric field is much weaker than this value. It is known that, if the Reynolds number (Re) is small, the shape of a drop remains spherical.[14,15] In our case, because the typical value of Re is on the order of $10^{-10} - 10^{-8}$, the deformation of droplet can be neglected. Consequently, the distribution of charge on the droplet surface is uniform, and the surface potential is position independent. The surface conductivity of the droplet is neglected, that is, the surface potential is represented by the ζ potential. Both the droplet fluid and the fluid in the cavity are incompressible and have constant physical properties.

Governing Equations

The governing equations for the present problem include those for the electric, concentration, and flow fields. For the fluid outside the droplet, these equations are

$$\nabla^2\phi = -\frac{\rho_e}{\epsilon} = -\sum_{j=1}^{2}\frac{z_j\hat{e}n_j}{\epsilon} \tag{1}$$

$$\frac{\partial n_j}{\partial t} = -\nabla\cdot\mathbf{f}_j \tag{2}$$

$$\mathbf{f}_j = -D_j\left(\nabla n_j + \frac{n_j\hat{e}z_j}{kT}\nabla\phi\right) + n_j\mathbf{u} \tag{3}$$

$$\nabla\cdot\mathbf{u} = 0 \tag{4}$$

$$\rho_o\frac{\partial\mathbf{u}}{\partial t} = -\nabla p + \eta_o\nabla^2\mathbf{u} - \rho_e\nabla\phi \tag{5}$$

In these expressions, ∇ and ∇^2 are respectively the gradient operator and the Laplace operator; ϕ is the electrical potential; ρ_e is the space charge density; ϵ is the permittivity of the fluid in the cavity; k and T are respectively the Boltzmann constant and the absolute temperature; $\hat{e}$ is the elementary charge; n_j, $\mathbf{f}_j$, and D_j are respectively the number concentration, the flux, and the diffusivity of the jth ionic species; $\mathbf{u}$ is the velocity of fluid; p is the pressure; ρ_o and η_o are respectively the density and the viscosity of the fluid in the cavity.

For the domain inside the droplet, since the fluid contains no electrolyte, only the flow field needs be solved. Because the Reynolds number is small we have

$$\nabla\cdot\mathbf{u} = 0 \tag{6}$$

$$\rho_i\frac{\partial\mathbf{u}}{\partial t} = -\nabla p + \eta_i\nabla^2\mathbf{u} \tag{7}$$

where ρ_i and η_i are respectively the density and the viscosity of the droplet fluid.

For convenience, all the dependent variables are partitioned into an equilibrium term (i.e., when the applied electric field is absent), and a perturbed term arises from the applied electric field. The symmetric nature of the present problem implies that the dependent variables are functions of r, θ, and t only. We have

$$\phi(r,\theta,t) = \phi_e(r) + \delta\phi(r,\theta)E_z e^{-i\omega t} \tag{8}$$

$$n_j(r,\theta,t) = n_j^e(r,\theta) + \delta n_j(r,\theta)E_z e^{-i\omega t} \tag{9}$$

$$\mathbf{u}(r,\theta,t) = 0 + \delta\mathbf{u}(r,\theta)E_z e^{-i\omega t} \tag{10}$$

$$p(r,\theta,t) = p_e(r,\theta) + \delta p(r,\theta)E_Z e^{-i\omega t} \tag{11}$$

In these expressions, the subscript and the superscript "e" denote the equilibrium properties, and δ denotes the perturbed properties. Note that, for the equilibrium case, since the droplet remains fixed when the applied electric field is absent, the velocity vanishes.

Equilibrium System

Since the distribution of ionic species at equilibrium follows Boltzmann distribution, the governing equation for ϕ_e is

$$\nabla^2\phi_e(r) = -\sum_{j=1}^{2}\frac{z_j\hat{e}n_{j0}^e}{\epsilon}\exp\left(-\frac{z_j\hat{e}\phi_e}{kT}\right) \tag{12}$$

where n_{j0}^e is the bulk number concentration of ionic species j. Suppose that both the potential on the droplet surface and that on the cavity surface are kept constant. Then the boundary conditions associated with eq 12 are

$$\phi_e = \zeta_a,\ r = a \tag{13}$$

$$\phi_e = \zeta_b,\ r = b \tag{14}$$

Perturbed System

Taking ∇^2 on both sides of eq 8 gives

$$\nabla^2(\delta\phi(r,\theta)E_z e^{-i\omega t}) = \nabla^2\phi(r,\theta,t) - \nabla^2\phi_e(r) \tag{15}$$

The governing equation for ϕ is assumed to take the form

$$\nabla^2\phi = -\sum_{j=1}^{2}\frac{z_j\hat{e}n_{j0}^e}{\epsilon}\exp\left(-\frac{z_j\hat{e}(\phi + g_jE_z e^{-i\omega t})}{kT}\right) \tag{16}$$

where the effect of double-layer deformation is taken into account by the function $g_jE_z e^{-i\omega t}$. Substituting eq 8 into this expression yields

---

(14) Saito, S. *Sci. Rep. Tohoku Imp. Univ. (Sendai, Jpn.)* **1913**, *2*, 179.
(15) Taylor, T. D.; Acrivos, A. *J. Fluid Mech.* **1964**, *18*, 466.

$$\nabla^2\phi = -\sum_{j=1}^{2}\frac{z_j\hat{e}n_{j0}^{\mathrm{e}}}{\epsilon}\exp\left(-\frac{z_j\hat{e}(\phi_{\mathrm{e}} + \delta\phi E_z\mathrm{e}^{-i\omega t} + g_jE_z\mathrm{e}^{-i\omega t})}{kT}\right) \quad (17)$$

Equations 1 and 17 lead to

$$n_j = n_{j0}^{\mathrm{e}}\exp\left(-\frac{z_j\hat{e}(\phi_{\mathrm{e}} + \delta\phi E_z\mathrm{e}^{-i\omega t} + g_jE_z\mathrm{e}^{-i\omega t})}{kT}\right) \quad (18)$$

Combining eqs 12, 15, and 17 yields the governing equation for $\delta\phi E_z\mathrm{e}^{-i\omega t}$:

$$\nabla^2(\delta\phi E_z\mathrm{e}^{-i\omega t}) = \sum_{j=1}^{2}\frac{z_j\hat{e}n_{j0}^{\mathrm{e}}}{\epsilon}\left(\exp\left(-\frac{z_j\hat{e}}{kT}(\phi_{\mathrm{e}} + \delta\phi E_z\mathrm{e}^{-i\omega t} + g_jE_z\mathrm{e}^{-i\omega t})\right) - \exp\left(-\frac{z_j\hat{e}}{kT}\phi_{\mathrm{e}}\right)\right) \quad (19)$$

The function $g_jE_z\mathrm{e}^{-i\omega t}$ can be determined by first combing eqs 2 and 3 to give

$$\frac{\partial n_j}{\partial t} = -D_j\left(\nabla^2 n_j + \frac{z_j\hat{e}}{kT}(\nabla n_j\cdot\nabla\phi + n_j\nabla^2\phi)\right) + \mathbf{u}\cdot\nabla n_j \quad (20)$$

Substituting eqs 8−10 into this expression and dividing both sides of the resultant expression by $E_z\mathrm{e}^{-i\omega t}$, we obtain

$$-i\omega\delta n_j = -D_j\Big\{\nabla^2(\delta n_j) + \frac{z_j\hat{e}}{kT}[\nabla n_j^{\mathrm{e}}\cdot\nabla(\delta n_j) + \nabla(\delta n_j)\cdot\nabla\phi_{\mathrm{e}} + \nabla(\delta n_j)\cdot\nabla(\delta\phi E_z\mathrm{e}^{-i\omega t}) + n_j^{\mathrm{e}}\nabla^2(\delta\phi) + (\delta n_j)\nabla^2\phi_{\mathrm{e}} + (\delta n_j)\nabla^2(\delta\phi E_z\mathrm{e}^{-i\omega t})]\Big\} + (\delta\mathrm{u})\cdot\nabla(n_j^{\mathrm{e}} + \delta n_jE_z\mathrm{e}^{-i\omega t}) \quad (21)$$

The equilibrium ionic concentration is $n_j^{\mathrm{e}} = n_{j0}^{\mathrm{e}}\exp(-z_j\hat{e}\phi_{\mathrm{e}}/kT)$, and the corresponding perturbed concentration can be determined from eqs 9 and 18. We have

$$\delta n_jE_z\mathrm{e}^{-i\omega t} = n_{j0}^{\mathrm{e}}\left[\exp\left(-\frac{z_j\hat{e}(\phi_{\mathrm{e}} + \delta\phi E_z\mathrm{e}^{-i\omega t} + g_jE_z\mathrm{e}^{-i\omega t})}{kT}\right) - \exp\left(-\frac{z_j\hat{e}\phi_{\mathrm{e}}}{kT}\right)\right] \quad (22)$$

Substituting eqs 18 and 22 into eq 21 yields the governing equation for g_j. For a simpler treatment, g_j, instead of δn_j, is solved in subsequent discussions.

Note that g_j needs to be solved simultaneously with the flow field. The fluid is stagnant in the absence of the applied electric field, and therefore, $\nabla p_{\mathrm{e}} = 0$ and $\mathbf{u}_{\mathrm{e}} = 0$, and only the perturbed flow field needs to be solved. Equations 4−8 and 10 yield

$$\nabla\cdot(\delta\mathrm{u}E_z\mathrm{e}^{-i\omega t}) = 0,\ 0 < r < b \quad (23)$$

$$-i\omega\rho_{\mathrm{o}}\delta\mathrm{u}E_z\mathrm{e}^{-i\omega t} = -\nabla\delta pE_z\mathrm{e}^{-i\omega t} + \eta_{\mathrm{o}}\nabla^2\delta\mathrm{u}E_z\mathrm{e}^{-i\omega t} - \rho_{\mathrm{e}}\nabla\phi,\ a < r < b \quad (24)$$

$$-i\omega\rho_{\mathrm{i}}\delta\mathrm{u}E_z\mathrm{e}^{-i\omega t} = -\nabla\delta pE_z\mathrm{e}^{-i\omega t} + \eta_{\mathrm{i}}\nabla^2\delta\mathrm{u}E_z\mathrm{e}^{-i\omega t},\ 0 < r < a \quad (25)$$

The mathematical treatments can be made simpler by employing a stream function representation ψ. In terms of ψ, the r and the θ components of $\delta\mathbf{u}$, δu_r and δu_θ, can be expressed respectively as $\delta u_r = -(1/r^2\sin\theta)(\partial\psi/\partial\theta)$ and $\delta u_\theta = (1/r\sin\theta)(\partial\psi/\partial r)$. We have

$$\delta\mathrm{u}E_z\mathrm{e}^{-i\omega t} = (\delta u_r\hat{r} + \delta u_\theta\hat{\theta})E_z\mathrm{e}^{-i\omega t} \quad (26)$$

Note that eq 23 is satisfied automatically by δu_r and δu_θ. Taking curl on both sides of eqs 24 and 25 to eliminate the pressure term and introducing ψ, we obtain

$$\eta_{\mathrm{o}}L^4\psi + i\omega\rho_{\mathrm{o}}L^2\psi = \left(\frac{\partial\rho_{\mathrm{e}}}{\partial r}\frac{\partial\phi}{\partial\theta} - \frac{\partial\rho_{\mathrm{e}}}{\partial\theta}\frac{\partial\phi}{\partial r}\right)\sin\theta,\ a < r < b \quad (27)$$

$$\eta_{\mathrm{i}}L^4\psi + i\omega\rho_{\mathrm{i}}L^2\psi = 0,\ 0 < r < a \quad (28)$$

where

$$L^2 = \left(\frac{\partial^2}{\partial r^2}\right) + \frac{\sin\theta}{r^2}\frac{\partial}{\partial\theta}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\right) \quad (29)$$

$$L^4 = L^2L^2 = \left[\left(\frac{\partial^2}{\partial r^2}\right) + \frac{\sin\theta}{r^2}\frac{\partial}{\partial\theta}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\right)\right]^2 \quad (30)$$

We assume that the surface of a droplet is impenetrable to ionic species, and therefore,

$$\nabla(\delta\phi E_z\mathrm{e}^{-i\omega t})\cdot\hat{\mathbf{n}} = 0,\ r = a \quad (31)$$

$$(\mathbf{f}_j - n_j\mathbf{u})\cdot\hat{\mathbf{n}} = 0,\ r = a \quad (32)$$

On the cavity surface, the electric field is that which arises from the applied electric field, and the ionic concentration reaches the equilibrium value, that is,

$$\frac{\partial(\delta\phi E_z\mathrm{e}^{-i\omega t})}{\partial r} = -E_z\mathrm{e}^{-i\omega t}\cos\theta,\ r = b \quad (33)$$

$$n_j = n_{j0}^{\mathrm{e}}\exp\left(-\frac{z_j\hat{e}}{kT}\phi_{\mathrm{e}}\right),\ r = b \quad (34)$$

The droplet surface is impenetrable to dispersion medium, and both the velocity and the shear stress are continuous on that surface. Therefore,

$$\delta u_rE_z\mathrm{e}^{-i\omega t}|_{r=a^+} = \delta u_rE_z\mathrm{e}^{-i\omega t}|_{r=a^-} = 0,\ r = a \quad (35)$$

$$\delta u_\theta E_z\mathrm{e}^{-i\omega t}|_{r=a^+} = \delta u_\theta E_z\mathrm{e}^{-i\omega t}|_{r=a^-},\ r = a \quad (36)$$

$$(\tau^{\mathbf{n}}\cdot\hat{\mathbf{n}})\times\hat{\mathbf{n}}|_{r=a^+} = (\tau^{\mathbf{n}}\cdot\hat{\mathbf{n}})\times\hat{\mathbf{n}}|_{r=a^-},\ \ r = a \quad (37)$$

where $\tau^{\mathbf{n}}$ is the shear stress tensor on the droplet surface. The relative velocity between the cavity and the droplet is $-UE_z\mathrm{e}^{-i\omega t}$, that is,

$$\delta u_rE_z\mathrm{e}^{-i\omega t} = -(U_{\mathrm{R}} + iU_{\mathrm{I}})E_z\mathrm{e}^{-i\omega t}\cos\theta,\ \ r = b \quad (38)$$

At the center of the droplet, we must have

$$\delta u_rE_z\mathrm{e}^{-i\omega t} = 0,\ \ r = 0 \quad (39)$$

$$\delta u_\theta E_z\mathrm{e}^{-i\omega t} = 0,\ \ r = 0 \quad (40)$$

For a simpler treatment, dimensionless quantities are used in subsequent discussions. On the basis of the scaling factors a, ζ_a,

n_{10}^{e}, and $U_{\mathrm{E}} = \epsilon\zeta_a{}^2/\eta_{\mathrm{o}}a$, we define the following dimensionless quantities: $E_z^* = E_z/(\zeta_a/a)$; $U^*E_z^*\mathrm{e}^{-i\omega t} = UE_z\mathrm{e}^{-i\omega t}/U_{\mathrm{E}}$; $\phi_{\mathrm{e}}^* = \phi_{\mathrm{e}}/\zeta_a$; $\delta\phi^*E_z^*\mathrm{e}^{-i\omega t} = \delta\phi E_z\mathrm{e}^{-i\omega t}/\zeta_a$; $g_j^*E_z^*\mathrm{e}^{-i\omega t} = g_jE_z\mathrm{e}^{-i\omega t}/\zeta_a$; $\psi^*E_z^*\mathrm{e}^{-i\omega t} = \psi\mathrm{E}_z\mathrm{e}^{-i\omega t}/U_{\mathrm{E}}a$; $n_j^* = n_j/n_{10}^{\mathrm{e}}$; and $r^* = r/a$. Since the applied electric field is relatively weak compared to that established by the droplet, $|E_z\mathrm{e}^{-i\omega t}| \ll (\zeta_a/a)$, which implies that $|\delta\phi E\mathrm{e}^{-i\omega t}| \ll \phi_{\mathrm{e}}$ and $|g_jE\mathrm{e}^{-i\omega t}| \ll \phi_{\mathrm{e}}$. Therefore, eq 18 can be approximated by

$$n_1^* = \exp(-\phi_r\phi_{\mathrm{e}}^*)[1 - \phi_r(\delta\phi^* + g_1^*)E_z^*\mathrm{e}^{-i\omega t}] \qquad (41)$$

and

$$n_2^* = \alpha\exp(\alpha\phi_r\phi_{\mathrm{e}}^*)[1 + \alpha\phi_r(\delta\phi^* + g_2^*)E_z^*\mathrm{e}^{-i\omega t}] \qquad (42)$$

where $\phi_r = z_1e\zeta_a/kT$ is the scaled surface potential.

Applying the method of separation of variables, we have

$$\begin{cases}\delta\phi^*(r,\theta) = (\Phi_{\mathrm{R}}(r) + i\Phi_{\mathrm{I}}(r))\cos\theta\\ g_1^*(r,\theta) = (G_{1\mathrm{R}}(r) + iG_{1\mathrm{I}}(r))\cos\theta\\ g_2^*(r,\theta) = (G_{2\mathrm{R}}(r) + iG_{2\mathrm{I}}(r))\cos\theta\\ \psi^*(r,\theta) = (\Psi_{\mathrm{R}}(r) + i\Psi_{\mathrm{I}}(r))\sin^2\theta\end{cases} \qquad (43)$$

where subscripts R and I respectively denote the real and the imaginary parts of a variable. Substituting these expressions into the corresponding governing equations yields

$$L_1{}^2\Phi_{\mathrm{R}} - \frac{(\kappa a)^2}{1+\alpha}[\exp(-\phi_r\phi_{\mathrm{e}}^*) + \alpha\exp(\alpha\phi_r\phi_{\mathrm{e}}^*)]\Phi_{\mathrm{R}} = \frac{(\kappa a)^2}{1+\alpha}[\exp(-\phi_r\phi_{\mathrm{e}}^*)G_{1\mathrm{R}} + \alpha\exp(\alpha\phi_r\phi_{\mathrm{e}}^*)G_{2\mathrm{R}}],\ a < r < b \qquad (44)$$

$$L_1{}^2\Phi_{\mathrm{I}} - \frac{(\kappa a)^2}{1+\alpha}[\exp(-\phi_r\phi_{\mathrm{e}}^*) + \alpha\exp(\alpha\phi_r\phi_{\mathrm{e}}^*)]\Phi_{\mathrm{I}} = \frac{(\kappa a)^2}{1+\alpha}[\exp(-\phi_r\phi_{\mathrm{e}}^*)G_{1\mathrm{I}} + \alpha\exp(\alpha\phi_r\phi_{\mathrm{e}}^*)G_{2\mathrm{I}}],\ a < r < b \qquad (45)$$

$$L_1{}^2G_{1\mathrm{R}} - \phi_r\frac{\mathrm{d}\phi_{\mathrm{e}}^*}{\mathrm{d}r^*}\frac{\mathrm{d}G_{1\mathrm{R}}}{\mathrm{d}r^*} + \mathrm{Pe}_1\frac{1}{r^{*2}}\Psi_{\mathrm{R}}\frac{\mathrm{d}\phi_{\mathrm{e}}^*}{\mathrm{d}r^*} - \frac{\omega a^2}{D_1}(\Phi_{\mathrm{I}} + G_{1\mathrm{I}}) = 0,\ a < r < b \qquad (46)$$

$$L_1{}^2G_{1\mathrm{I}} - \phi_r\frac{\mathrm{d}\phi_{\mathrm{e}}^*}{\mathrm{d}r^*}\frac{\mathrm{d}G_{1\mathrm{I}}}{\mathrm{d}r^*} + \mathrm{Pe}_1\frac{1}{r^{*2}}\Psi_{\mathrm{I}}\frac{\mathrm{d}\phi_{\mathrm{e}}^*}{\mathrm{d}r^*} + \frac{\omega a^2}{D_1}(\Phi_{\mathrm{R}} + G_{1\mathrm{R}}) = 0,\ a < r < b \qquad (47)$$

$$L_1{}^2G_{2\mathrm{R}} + \alpha\phi_r\frac{\mathrm{d}\phi_{\mathrm{e}}^*}{\mathrm{d}r^*}\frac{\mathrm{d}G_{2\mathrm{R}}}{\mathrm{d}r^*} + \mathrm{Pe}_2\frac{1}{r^{*2}}\Psi_{\mathrm{R}}\frac{\mathrm{d}\phi_{\mathrm{e}}^*}{\mathrm{d}r^*} - \frac{\omega a^2}{D_2}(\Phi_{\mathrm{I}} + G_{2\mathrm{I}}) = 0,\ a < r < b \qquad (48)$$

$$L_1{}^2G_{2\mathrm{I}} + \alpha\phi_r\frac{d\phi_{\mathrm{e}}^*}{\mathrm{d}r^*}\frac{\mathrm{d}G_{2\mathrm{I}}}{\mathrm{d}r^*} + \mathrm{Pe}_2\frac{1}{r^{*2}}\Psi_{\mathrm{I}}\frac{\mathrm{d}\phi_{\mathrm{e}}^*}{\mathrm{d}r^*} + \frac{\omega a^2}{D_2}(\Phi_{\mathrm{R}} + G_{2\mathrm{R}}) = 0,\ a < r < b \qquad (49)$$

$$L_2{}^4\Psi_{\mathrm{R}} - \frac{\rho_{\mathrm{o}}\omega a^2}{\eta_{\mathrm{o}}}L_2{}^2\Psi_{\mathrm{I}} = -\frac{(\kappa a)^2}{(1+\alpha)}(G_{1\mathrm{R}}\exp(-\phi_r\phi_{\mathrm{e}}^*) + \alpha G_{2\mathrm{R}}\exp(\alpha\phi_r\phi_{\mathrm{e}}^*))\frac{\mathrm{d}\phi_{\mathrm{e}}^*}{\mathrm{d}r^*},\ a < r < b \qquad (50)$$

$$L_2{}^4\Psi_{\mathrm{I}} + \frac{\rho_{\mathrm{o}}\omega a^2}{\eta_{\mathrm{o}}}L_2{}^2\Psi_{\mathrm{R}} = -\frac{(\kappa a)^2}{(1+\alpha)}(G_{1\mathrm{I}}\exp(-\phi_r\phi_{\mathrm{e}}^*) + \alpha G_{2\mathrm{I}}\exp(\alpha\phi_r\phi_{\mathrm{e}}^*))\frac{\mathrm{d}\phi_{\mathrm{e}}^*}{\mathrm{d}r^*},\ a < r < b \qquad (51)$$

$$L_2{}^4\Psi_{\mathrm{R}} - \frac{\rho_{\mathrm{o}}\omega a^2}{\eta_{\mathrm{o}}}\left(\frac{\eta_{\mathrm{o}}}{\eta_{\mathrm{i}}}\right)\left(\frac{\rho_{\mathrm{i}}}{\rho_{\mathrm{o}}}\right)L_2{}^2\Psi_{\mathrm{I}} = 0,\ 0 < r < a \qquad (52)$$

$$L_2{}^4\Psi_{\mathrm{I}} + \frac{\rho_{\mathrm{o}}\omega a^2}{\eta_{\mathrm{o}}}\left(\frac{\eta_{\mathrm{o}}}{\eta_{\mathrm{i}}}\right)\left(\frac{\rho_{\mathrm{i}}}{\rho_{\mathrm{o}}}\right)L_2{}^2\Psi_{\mathrm{R}} = 0,\ 0 < r < a \qquad (53)$$

In these expressions, $L_1{}^2 = (\mathrm{d}^2/\mathrm{d}r^{*2}) + (2/r^{*2})(\mathrm{d}/\mathrm{d}r^*) - (2/r^{*2})$, $L_2{}^4 = L_2{}^2L_2{}^2$, and $L_2{}^2 = (\mathrm{d}^2/\mathrm{d}r^{*2}) - (2/r^{*2})$; $\kappa^{-1} = (\epsilon kT/\Sigma_{j=1}^2 n_{j0}^e(ez_j)^2)^{1/2}$ is the Debye length; and $\mathrm{Pe}_j = U_{\mathrm{E}}a/D_j$ is the electric Peclet number of ionic species j. $(\rho_{\mathrm{o}}\omega a^2/\eta_{\mathrm{o}})$ is a measure of the relative significance between the dynamic inertial force and the viscous force, $(\omega a^2/D_j)$ is a measure of the relative significance between the rate of transport of ionic species j arising from the applied electric field and that due to diffusion. The associated boundary conditions are

$$\begin{cases}\dfrac{\partial\Phi_{\mathrm{R}}}{\partial r^*} = 0,\ r^* = 1\\ \dfrac{\partial\Phi_{\mathrm{R}}}{\partial r^*} = -E_z^*,\ r^* = \dfrac{b}{a}\end{cases} \qquad (54)$$

$$\begin{cases}\dfrac{\partial\Phi_{\mathrm{I}}}{\partial r^*} = 0,\ r^* = 1\\ \dfrac{\partial\Phi_{\mathrm{I}}}{\partial r^*} = 0,\ r^* = \dfrac{b}{a}\end{cases} \qquad (55)$$

$$\begin{cases}\dfrac{\mathrm{d}G_{1\mathrm{R}}}{\mathrm{d}r^*} = 0,\ r^* = 1\\ G_{1\mathrm{R}} = -\Phi_{\mathrm{R}},\ r^* = \dfrac{b}{a}\end{cases} \qquad (56)$$

$$\begin{cases}\dfrac{\mathrm{d}G_{1\mathrm{I}}}{\mathrm{d}r^*} = 0,\ r^* = 1\\ G_{1\mathrm{I}} = -\Phi_{\mathrm{I}},\ r^* = \dfrac{b}{a}\end{cases} \qquad (57)$$

$$\begin{cases}\dfrac{\mathrm{d}G_{2\mathrm{R}}}{\mathrm{d}r^*} = 0,\ r^* = 1\\ G_{2\mathrm{R}} = -\Phi_{\mathrm{R}},\ r^* = \dfrac{b}{a}\end{cases} \qquad (58)$$

$$\begin{cases}\dfrac{\mathrm{d}G_{2\mathrm{I}}}{\mathrm{d}r^*} = 0,\ r^* = 1\\ G_{2\mathrm{I}} = -\Phi_{\mathrm{I}},\ r^* = \dfrac{b}{a}\end{cases} \qquad (59)$$

$$\begin{cases} \Psi_R = 0, & r^* = 0 \\ \dfrac{d\Psi_R}{dr^*} = 0 & r^* = 0 \\ \Psi_R|_{r^*=1^+} = \Psi_R|_{r^*=1^-} = 0, & r^* = 1 \\ \left.\dfrac{d\Psi_R}{dr^*}\right|_{r^*=1^+} = \left.\dfrac{d\Psi_R}{dr^*}\right|_{r^*=1^-} & r^* = 1 \\ \left.\dfrac{d}{dr^*}\left(\dfrac{1}{r^{*2}}\dfrac{d\Psi_R}{dr^*}\right)\right|_{r^*=1^+} = \dfrac{\eta_i}{\eta_o}\left.\dfrac{d}{dr^*}\left(\dfrac{1}{r^{*2}}\dfrac{d\Psi_R}{dr^*}\right)\right|_{r^*=1^-}, & r^* = 1 \\ \Psi_R = \dfrac{1}{2}U_R r^*, & r^* = \dfrac{b}{a} \\ \dfrac{\partial\Psi_R}{\partial r^*} = U_R r^*, & r^* = \dfrac{b}{a} \end{cases} \tag{60}$$

$$\begin{cases} \Psi_I = 0, & r^* = 0 \\ \dfrac{d\Psi_I}{dr^*} = 0 & r^* = 0 \\ \Psi_I|_{r^*=1^+} = \Psi_I|_{r^*=1^-} = 0 & r^* = 1 \\ \left.\dfrac{d\Psi_I}{dr^*}\right|_{r^*=1^+} = \left.\dfrac{d\Psi_I}{dr^*}\right|_{r^*=1^-} & r^* = 1 \\ \left.\dfrac{d}{dr^*}\left(\dfrac{1}{r^{*2}}\dfrac{d\Psi_I}{dr^*}\right)\right|_{r^*=1^+} = \dfrac{\eta_i}{\eta_o}\left.\dfrac{d}{dr^*}\left(\dfrac{1}{r^{*2}}\dfrac{d\Psi_I}{dr^*}\right)\right|_{r^*=1^-} & r^* = 1 \\ \Psi_I = \dfrac{1}{2}U_I r^* & r^* = \dfrac{b}{a} \\ \dfrac{\partial\Psi_I}{\partial r^*} = U_I r^* & r^* = \dfrac{b}{a} \end{cases} \tag{61}$$

The scaled governing equations for the equilibrium potential and the associated boundary conditions are

$$\frac{1}{r^{*2}}\frac{d}{dr^*}\left(r^{*2}\frac{d\phi_e^*}{dr^*}\right) = -\frac{(\kappa a)^2}{(1+\alpha)\phi_r}(\exp(-\phi_r\phi_e^*) - \exp(\alpha\phi_r\phi_e^*)) \tag{62}$$

$$\begin{cases} \phi_e^* = 1, \ r^* = 1 \\ \phi_e^* = \dfrac{\zeta_b}{\zeta_a}, \ r^* = \dfrac{b}{a} \end{cases} \tag{63}$$

For the present problem, the dynamic electrophoretic mobility of droplet μ is defined as

$$\mu = \mu_R + i\mu_I = \frac{U}{E} \tag{64}$$

where $E = E_z e^{-i\omega t}$ and $U = (U_R + iU_I)E_z e^{-i\omega t}$, with μ_R and μ_I respectively being the real and imaginary parts of μ, which can be determined from a force balance on a droplet. The z components of the forces acting on a droplet include the electric force F_e and the hydrodynamic drag F_h. According to the Newtonian second law of motion,

$$F_h + F_e = \frac{4}{3}\pi a^3(\rho_i - \rho_o)\frac{dU}{dt} \tag{65}$$

In terms of scaled quantities, it can be shown that this expression can be rewritten as

$$F_h^* + F_e^* = -i\left(\frac{4}{3}\pi\epsilon\zeta^2\right)\left(\frac{\rho_o\omega a^2}{\eta_o}\right)\left(\frac{\rho_i - \rho_o}{\rho_o}\right)(U_R^* + iU_I^*)E_z^* e^{-i\omega t} \tag{66}$$

F_e can be evaluated by

$$F_e = \int\int_{r=a}\sigma(-\nabla\phi)_s \cdot \mathbf{e}_z dS \tag{67}$$

where the surface charge density σ can be determined from Gauss law as

$$q = \int\int\epsilon(\mathbf{E}\cdot\hat{\mathbf{n}})dS = \int\int\sigma dS \tag{68}$$

where q is the total amount of charge enclosed by surface S, and $\mathbf{E} = -\nabla\phi$. Substituting eq 68 into eq 67 and using the relation $dS = 2\pi r^2 \sin\theta d\theta$, it can be shown that

$$F_e^* = \frac{8}{3}\pi\epsilon\zeta_a^{\ 2}\left[r^*\frac{dF_e^*\,\phi_e^*}{dr^*}(\Phi_R + i\Phi_I)E_z^* e^{-i\omega t}\right]_{r^*=1} \tag{69}$$

This expression implies that knowing ϕ_e^*, Φ_R, and Φ_I suffices the determination of F_e^*.

Applying the result of Happel and Brenner,[16] F_h can be expressed as

$$F_h = -\pi\rho_o\int_0^\pi\left[r^2\sin\theta\frac{\partial}{\partial t}\left(\frac{\partial(\psi E_z e^{-i\omega t})}{\partial r}\right)\right]_s d\theta + \eta\pi\int_0^\pi\left[r^4\sin^3\frac{\partial}{\partial r}\left(\frac{E^2\psi E_z e^{-i\omega t}}{r^2\sin^2\theta}\right)\right]_s d\theta - \pi\int_0^\pi\left[r^2\sin^2\theta\rho_e\frac{\partial\phi}{\partial\theta}\right]_s d\theta \tag{70}$$

The first term on the right-hand side of this expression is the force arising from the change of the momentum of fluid, the second term is the drag on a droplet, and the third term is the electric force arising from the flow of electrolyte solution. Applying the relation $\partial\phi_e^*/\partial\theta = 0$, it can be shown that

$$F_h^* = \pi\epsilon\zeta_a^{\ 2} i\left(\frac{\omega\rho_o a^2}{\eta_o}\right)\int_0^\pi\left[r^{*2}\sin\theta\frac{\partial(\psi^* E_z^* e^{-i\omega t})}{\partial r^*}\right]_{r^*=1} d\theta + \pi\epsilon\zeta_a^{\ 2}\int_0^\pi\left[r^{*4}\sin^3\theta\frac{\partial}{\partial r^*}\left(\frac{E^{*2}\psi^* E_z^* e^{-i\omega t}}{r^{*2}\sin^2\theta}\right)\right]_{r^*=1} d\theta - \pi\epsilon\zeta_a^{\ 2}\frac{(\kappa a)^2}{(1+\alpha)\phi_r}\int_0^\pi\left[r^{*2}\sin^2\theta(\exp(-\phi_r\phi_e^*) - \exp(\alpha\phi_r\phi_e^*))\frac{\partial\delta\phi^*}{\partial\theta}E_z^* e^{-i\omega t}\right]_{r^*=1} d\theta \tag{71}$$

This expression implies that knowing ϕ_e^*, Φ_R, Φ_I, Ψ_R, and Ψ_I suffices the determination of F_h^*.

To avoid tedious recursive procedure in the evaluation of dynamic mobility, the present problem is divided into two subproblems. In the first one, a droplet moves with a scaled velocity $(U_R^* + iU_I^*)E_z^* e^{-i\omega t}$ in the absence of the applied electric field, and, in the second one, a scaled electric field $E_z^* e^{-i\omega t}$ is applied, but a droplet is fixed in space. Note that the partition of the present problem is for a simpler mathematical treatment; the two subproblems have no actual physical meaning. The linear nature of the present problem implies that the scaled total force

---

[16] Happel, J.; Brenner, H. *Low-Reynolds Number Hydrodynamics*; Nijhoff: Boston, MA, 1983.

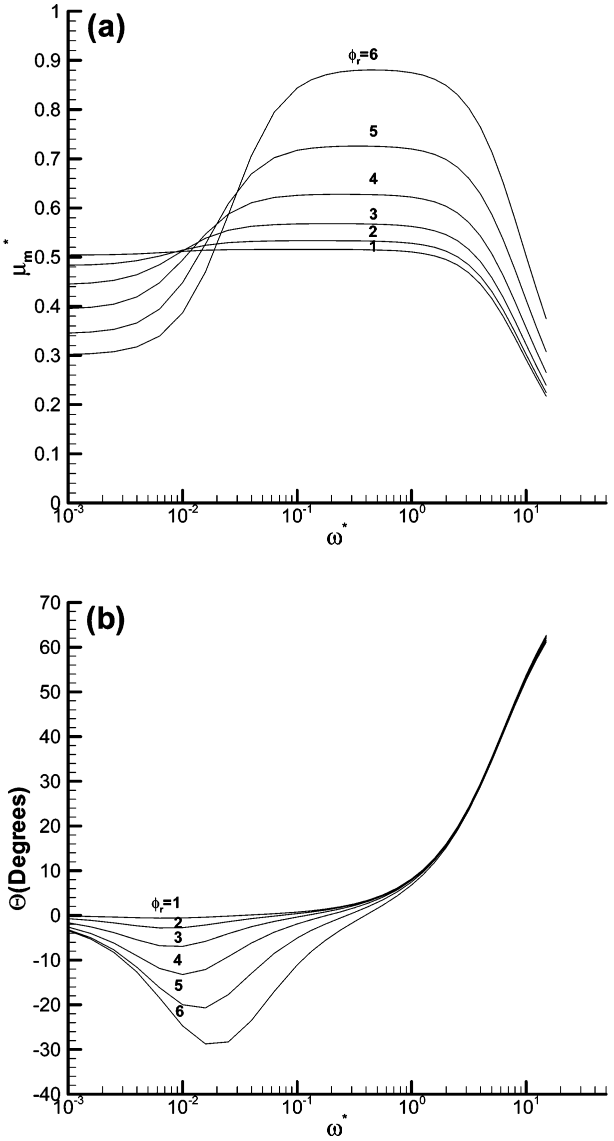


Figure 2. Variation in the scaled magnitude of electrophoretic mobility μ_m^* (a) and phase angle Θ (b) as a function of scaled frequency ω^* for various ϕ_r at $\kappa a = 1$, $H = 0.1$, and $\eta_o/\eta_i = 1$.

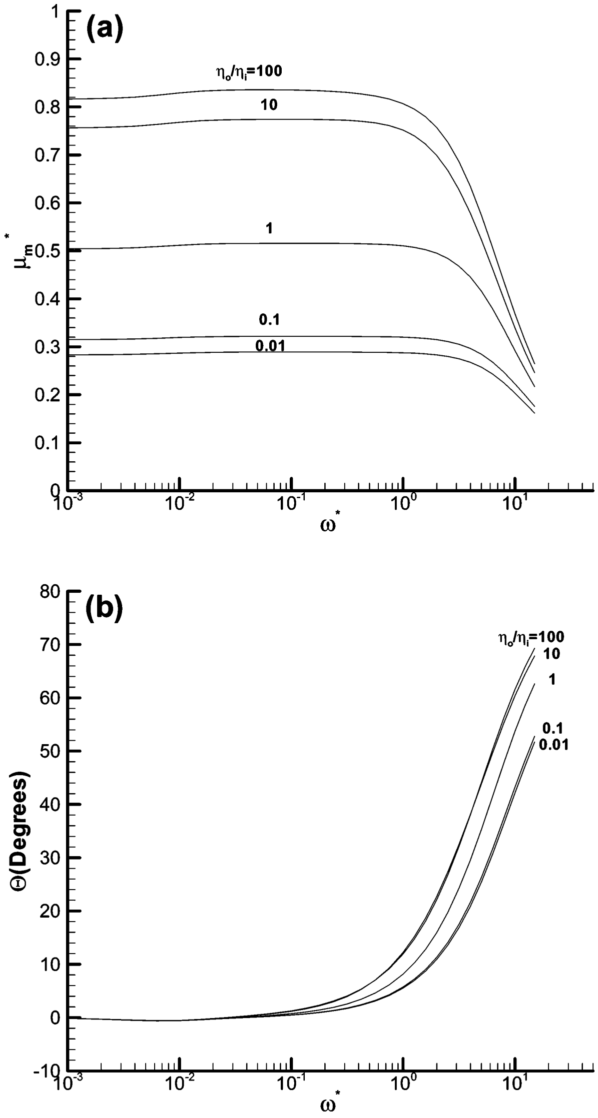


Figure 3. Variation in the scaled magnitude of electrophoretic mobility μ_m^* (a) and phase angle Θ (b) as a function of scaled frequency ω^* for various η_o/η_i at $\kappa a = 1$, $H = 0.1$, and $\phi_r = 1$.

acting on a droplet in the first subproblem, F_1^*, is proportional to $(U_R^* + iU_I^*)E_z^* e^{-i\omega t}$, and that in the second subproblem, F_2^*, is proportional to $E_z^* e^{-i\omega t}$. That is,

$$F_1^* = \chi(U_R^* + iU_I^*)E_z^* e^{-i\omega t} \tag{72}$$

$$F_2^* = \beta E_z^* e^{-i\omega t} \tag{73}$$

where χ and β are complex constants. Therefore, eq 65 can be rewritten as

$$F_h^* + F_e^* = F_1^* + F_2^* = -i\left(\frac{4}{3}\pi\epsilon\zeta_a^{\,2}\right)\left(\frac{\rho_o\omega a^2}{\eta_o}\right)\left(\frac{\rho_i - \rho_o}{\rho_o}\right)(U_R^* + iU_I^*)E_z^* e^{-i\omega t} \tag{74}$$

Equations 64 and 72−74 yield

$$\mu^* = \frac{-\beta}{\chi + i(\rho_o\omega a^2/\eta_o)[(\rho_i - \rho_o)/\rho_o]} \tag{75}$$

where $\mu^* = \mu/(\epsilon\zeta_a/\eta_o)$. Therefore, knowing the values of χ and β suffices the determination of the dynamic mobility, and no recursive procedure is necessary. Note that these complex constants are independent of the applied electric field and the velocity of a droplet. For the present problem, the electrophoretic velocity is complex, and we define the scaled magnitude of the mobility μ_m^* as $\mu_m^* = \sqrt{\mu_R^{\,2} + \mu_I^{\,2}}$ and the corresponding phase angle Θ as $\Theta = \tan^{-1}(\mu_I/\mu_R)$, that is, $\mu^* = \mu_m^* e^{i\Theta}$. Here, Θ measures the phase difference between **U** and **E**; a negative Θ implies that **U** leads **E**, and the reverse is true if Θ is positive.

The governing equations and the associated boundary conditions are solved numerically by a pseudospectral method based on Chebyshev polynomials. This approach has been justified to be accurate and efficient for the electrokinetic phenomenon of the present type.[17,18]

Results and Discussion

Numerical simulations are conducted to examine the influences of the key parameters of the system under consideration on the

---

[17] Lee, E.; Chu, J. W.; Hsu, J. P. *J. Colloid Interface Sci.* **1998**, *205*, 65.
[18] Lee, E.; Chu, J. W.; Hsu, J. P. *J. Colloid Interface Sci.* **1999**, *209*, 240.

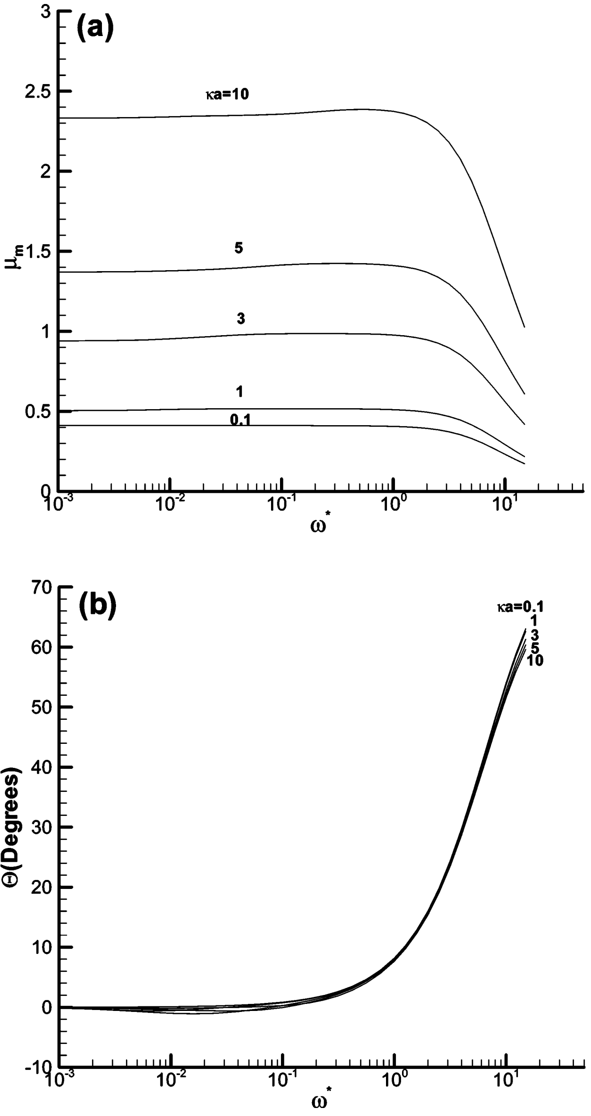


Figure 4. Variation in the scaled magnitude of electrophoretic mobility μ_m^* (a) and phase angle Θ (b) as a function of scaled frequency ω^* for various κa at $\phi_r = 1$, $H = 0.1$, and $\eta_o/\eta_i = 1$.

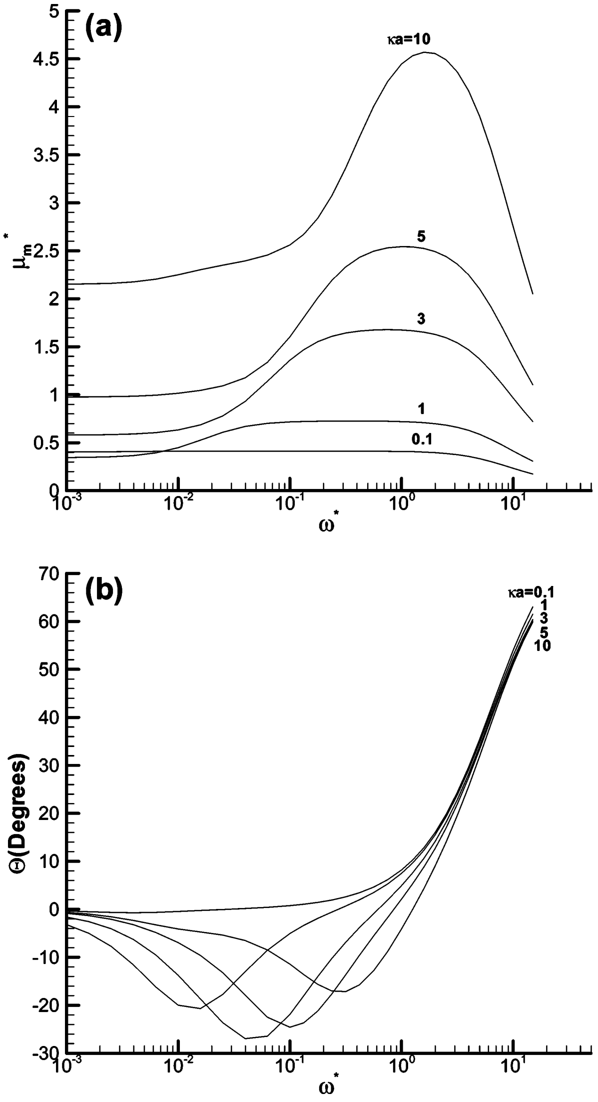


Figure 5. Variation in the scaled magnitude of electrophoretic mobility μ_m^* (a) and phase angle Θ (b) as a function scaled frequency ω^* for various κa at $\phi_r = 5$, $H = 0.1$, and $\eta_o/\eta_i = 1$.

electrophoretic behavior of a droplet. These include $(\omega a^2/D_1)$, $(\omega a^2/D_2)$, Pe_1, Pe_2, κa, (ρ_i/ρ_o), (η_o/η_i), ϕ_r, $H = (a/b)^3$, and the scaled frequency of the applied electric field $\omega^* = \rho_o\omega a^2/\eta_o$. The following values, which are based on an aqueous KCl solution at 298.15 K, are chosen: $\epsilon = 8.854 \times 10^{-12} \times 78.54688$ F m^{-1}; $\eta_o = 0.8904$ cp; $\rho_o = 0.99704$ g/cm^3, $Z_1 = 1$; $Z_2 = -1$; $D_1 = 1.962297 \times 10^{-5}$ cm^2/s; and $D_2 = 2.037051 \times 10^{-5}$ cm^2/s. These values yield $\omega a^2/D_1 = 454.88(\rho_o\omega a^2/\eta_o)$ and $\omega a^2/D_2 = 472.21(\rho_o\omega a^2/\eta_o)$. Also, we assume $(\rho_i - \rho_o)/\rho_o = 0.1$ and $Pe_1 = Pe_2 = 0.01$.

Influence of Surface Potential. The variations of the scaled magnitude of the dynamic mobility of a droplet μ_m^* and the corresponding phase angle Θ as a function of the scaled frequency of the applied electric field ω^* at various levels of the scaled surface potential ϕ_r are presented in Figure 2. For the case in which ϕ_r is low, μ_m^* decreases and Θ, which is positive, increases with the increase in ω^*. The former is because, as ω^* increases, the time interval available for the acceleration of a droplet becomes short. The latter is because, if ϕ_r is low, the deformation of the double layer surrounding a droplet is negligible; therefore, the higher the frequency, the greater its inertia and the slower its response to the applied electric field. As ϕ_r increases and the thickness of double layer is on the order of the radius of the droplet ($\kappa a = 1$), μ_m^* shows a local maximum and Θ has a negative (phase lead) local minimum as ω^* varies. These arise from the effect of double-layer deformation, which yields an induced electric field near the droplet. When an external electric field is applied, since this induced electric field is in the opposite direction of that of the applied electric field, it has the effect of retarding the movement of a droplet. However, when the applied electric field changes its direction, if the redistribution of the ionic species in the double layer is not fast enough, the induced electric field becomes advantageous to the movement of a droplet. The presence of the local maximum in μ_m^* and the phase lead become inappreciable if ω^* is sufficiently high. This is because, if ω^* is high, the change in the direction of the movement of the droplet is fast, and the deformation of the double layer becomes inappreciable.

Influence of Droplet Viscosity. The influence of the relative viscosity of the droplet fluid, measured by the ratio η_o/η_i, on its electrophoretic behavior for the case in which ϕ_r is low is illustrated in Figure 3. Note that, as $\eta_o/\eta_i \rightarrow 0$, the behavior of a droplet approaches that of a rigid particle, and, as $\eta_o/\eta_i \rightarrow \infty$,

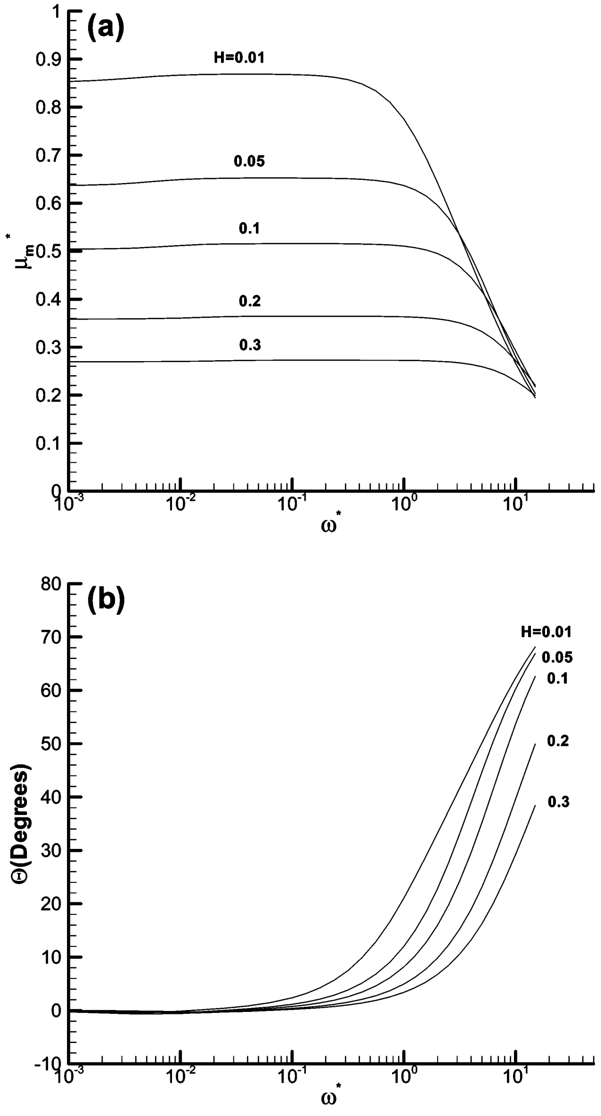


Figure 6. Variation in the scaled magnitude of electrophoretic mobility μ_m^* (a) and phase angle Θ (b) as a function of scaled frequency ω^* for various H at $\phi_r = 1$, $\kappa a = 1$, and $\eta_o/\eta_i = 1$.

its behavior approaches that of a gas bubble. Figure 3 reveals that, in general, μ_m^* increases with the increase in η_o/η_i, so it is the phase lag. This is expected because the larger the value of η_o/η_i, the smaller the hydrodynamic drag acting on the droplet.

Influence of Double-Layer Thickness. Figures 4 and 5 show the influence of the thickness of the double layer surrounding a droplet, measured by κa, on its electrophoretic behavior at various levels of ϕ_r. In general, for a fixed value of ω^*, μ_m^* increases with the increase in κa. This is because the thinner the double layer surrounding a droplet, the greater the absolute value of the potential gradient on its surface, and, therefore, the greater the electrical driving force for its movement. Figures 4 and 5 indicate that, if ϕ_r is sufficiently high and the double layer is not thick, μ_m^* has a local maximum and Θ has a negative (phase lead) local minimum as ω^* varies. As pointed out previously, these arise from the effect of double-layer deformation. Note that the phase lag occurring at a medium to high value of ω^* decreases with the increase in κa. This is because, as the double layer becomes thinner, it is easier for a droplet to catch up to the variation of the applied electric field.

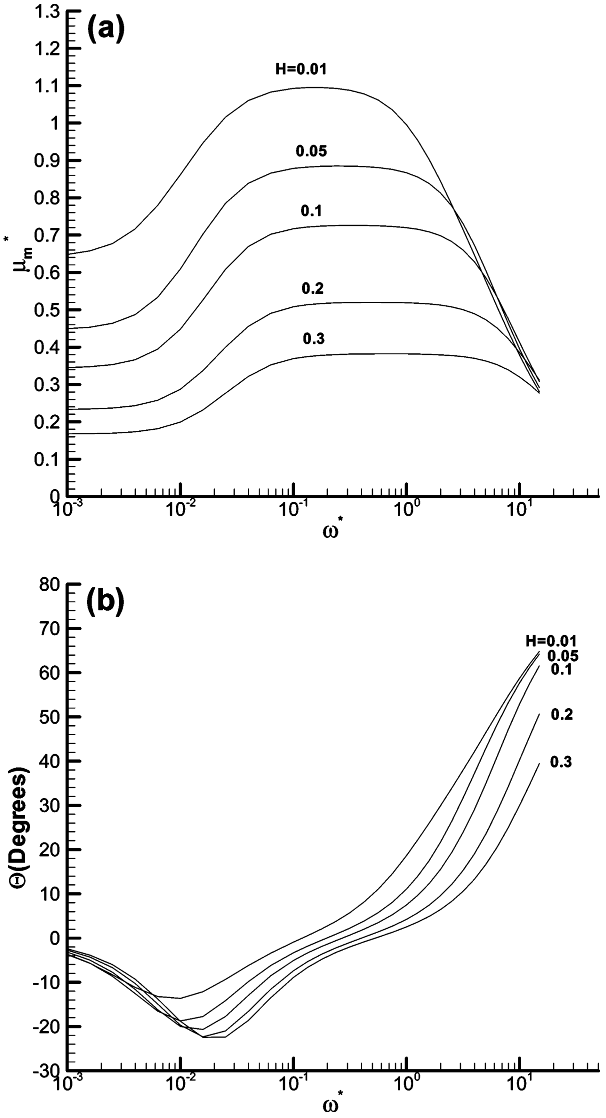


Figure 7. Variation in the scaled magnitude of electrophoretic mobility μ_m^* (a) and phase angle Θ (b) as a function of scaled frequency ω^* for various H at $\phi_r = 5$, $\kappa a = 1$, and $\eta_o/\eta_i = 1$.

Influence of Cavity Size. The influences of the relative size of a cavity, measured by H, on the electrophoretic behavior of a droplet at various levels of ϕ_r are illustrated in Figures 6 and 7. These figures indicate that μ^*_m declines with the increase in H. This is because the larger the value of H, the closer a droplet is to a cavity, and the greater the hydrodynamic retardation. Figure 7 reveals that, as H increases, the phase lead occurring at a low to medium value of ω^* becomes less appreciable. This is because the larger the value of H, the smaller the space available for double-layer deformation, and, therefore, its influence on the electrophoretic behavior of a droplet is confined. The behavior of the phase lag occurring at a medium to high value of ω^* can be interpreted by similar reasoning.

Conclusions

The boundary effect on the dynamic electrophoresis of a droplet is investigated by considering an electrolyte-free droplet in a spherical cavity. The influences of the frequency of the applied electric field, the thickness of the double layer surrounding a droplet, the relative size of a cavity, and the physical properties of a droplet on its electrophoretic behavior are discussed. We show that, if the deformation of the double layer is significant, the magnitude of the electrophoretic mobility of a droplet has a local maximum and the phase angle has a negative (phase lead) local minimum as the frequency of the applied electric field varies. The more important the boundary effect, the less significant the effect of double-layer deformation. In general, the smaller the viscosity of the fluid of a droplet, the larger the magnitude of its mobility.

Acknowledgment. This work is supported by the National Science Council of the Republic of China.

LA0533821