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Journal of Colloid and Interface Science 260 (2003) 118–125

Journal of Colloid and Interface Science

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Dynamic electrophoretic mobility of a sphere in a spherical cavity

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Received 13 August 2002; accepted 5 December 2002

Abstract

Dynamic electrophoresis is a powerful analytical tool for the description of the surface properties of the charged entities in a concentrated dispersion. In our study the boundary effect on this dynamic phenomenon is investigated theoretically for the case, when the surface potential is low. In particular, the dynamic electrophoresis of a sphere in a spherical cavity is discussed as are the effects of the key factors on the phenomenon under consideration, which include the thickness of the double layer, the frequency of the applied electric field, the ratio of particle radius to cavity radius, and the boundary conditions of the surfaces of the particle and the cavity. The results of numerical simulation reveal that these key factors can have both quantitative and qualitative influence on the electrophoretic behavior of the particle. As an example, for the case of a positively charged particle placed in a negatively charged cavity if the double layer surrounding the particle is thin, the magnitude of the electrophoretic mobility of the particle increases with an increase in the frequency of the applied electric field and a phase lead may occur, but the opposite is true if the double layer is thick. These effects are not observed for the case of a positively charged particle placed in an uncharged cavity or for a positively charged particle placed in a positively charged cavity.

Keywords: Electrophoresis, dynamic; Boundary effect, sphere in spherical cavity; Double-layer thickness, arbitrary; Surface potential, low; Applied electric field, frequency, phase angle

1. Introduction

When a sound wave passes through an electrolyte solution, a dynamic electric field will be induced. This phenomenon is observed for the case of a colloidal dispersion, the so-called colloid vibration potential (CVP) effect. Although the CVP effect was investigated extensively, its development was limited due to the lack of an appropriate experimental apparatus for its quantification. The problem remained unsolved until around 1980 when several devices become available. One of these is that used to measure the inverse effect of CVP; that is, a dynamic electric field is applied to a colloidal dispersion to induce a sound wave, the so-called electrokinetic sonic amplitude (ESA) effect. For both CVP and ESA effects, the frequency of the applied electric field is the same as that of the response frequency. The combination of CVP and ESA effects is called the electroacoustic effect by O'Brien [1]. He analyzed theoretically the dynamic electrophoretic mobility for the case of high surface potential and dilute dispersion, and he showed that an inverse relation exists between CVP and ESA. Corresponding experimental work was also conducted in which the surface potential of a particle was estimated based on electroacoustic measurement. A thorough review of the experimental development was provided by Hunter [2]. In the theoretical counterpart, Sawatzky and Babchin [3] were able to derive an approximate expression for the dynamic electrophoretic mobility for the case of low surface potential and arbitrary double layer thickness. Applying the numerical method of O'Brien [1], Magelsdorf and White [4] obtained an approximate numerical solution for the general electrokinetic equations for the case of a spherical particle at low potential but with a relatively thick double layer. Ohshima [5] derived a more accurate analytical expression for the electrophoretic mobility for the case of low potential and arbitrary double layer thickness.

These discussions focused mainly on the dynamic behavior of particles in an infinite fluid. In practice, however, the presence of a boundary is almost always inevitable. The wall of a container, for instance, may be important for the movement of nearby particles. The porosity of a porous medium should be considered in the modeling of the motion of a particle passing through it. A concentrated dispersion is another

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0021-9797/03/$ – see front matter
doi:10.1016/S0021-9797(02)00186-8

typical example, in which the neighboring particles can be viewed as a boundary. The effect of the presence of a boundary on the electrophoretic behavior of a particle for the case when a static electric field is applied has been examined by many investigators [6–12]. In the present study, we examine the boundary effect on the electrophoretic behavior of a particle for the case when a dynamic electric field is applied. We choose to work on the problem of the electrophoresis of a spherical particle in a spherical cavity. Although this is an idealized problem, which considerably simplifies the mathematical analysis, it provides valuable information about the presence of a rigid boundary on the behavior of a particle [7].

2. Theory

Referring to Fig. 1, we consider a spherical particle of radius a in a concentric spherical cavity of radius b. Let $H = a/b$. Spherical coordinates (r, Θ, φ) with the origin located at the center of the particle is adopted. The gap between the particle and the cavity contains an electrolyte solution, which is assumed to be Newtonian. An alternating electric field of strength $E_z e^{-i\omega t}$ and in a direction parallel to that represented by $\Theta = 0$ is applied, where ω is the frequency of the electric field and t is time. As a result, the particle has a velocity of magnitude $Ue^{-i\omega t}$. The so-called dynamic electrophoretic mobility $|\mu|$ is defined by $|\mu| = |\mathbf{U}|/|\mathbf{E}|$, where μ, $\mathbf{U}$, and $\mathbf{E}$ are complex numbers, in general. The conservation of ionic species j leads to

$$\frac{\partial n_j}{\partial t} = \nabla \cdot \left(-D_j \left(\nabla n_j + \frac{n_j e z_j}{k_B T} \nabla \phi \right) + n_j \mathbf{u} \right), \tag{1}$$

where n_j, D_j, and z_j are respectively the concentration, diffusion coefficient, and valence of ionic species j, e is

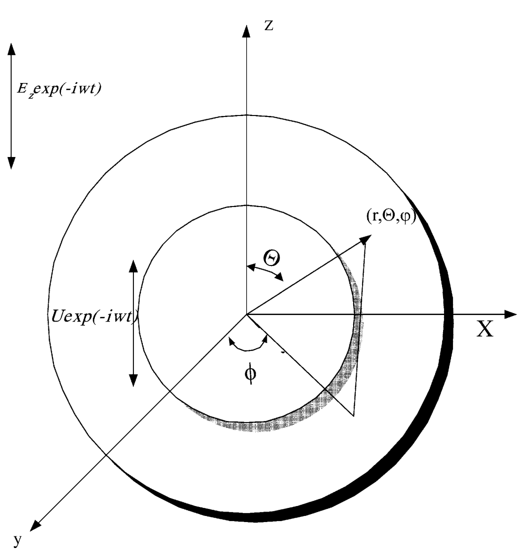

Fig. 1. Schematic representation of the problem under consideration. A particle of radius a is placed at the center of a spherical cavity of radius b. The cavity is filled with an electrolyte solution. **E** and **U** are the applied electric field and the velocity of fluid, respectively.

the elementary charge, ϕ is electrical potential, k_B is the Boltzmann constant, T is the absolute temperature, and $\mathbf{u}$ is the velocity of ions.

Suppose that the spatial variation in electrical potential can be described by the Poisson equation

$$\nabla^2 \phi = -\frac{\rho_e}{\varepsilon} = -\sum_{j=1}^{N} \frac{z_j e n_j}{\varepsilon}, \tag{2}$$

where ε is the permittivity, ρ_e is the space charge density, and N is the number of ionic species.

Suppose that the flow field can be described by the Navier–Stokes equation. For an incompressible fluid in the creeping flow regime, we have

$$\nabla \cdot \mathbf{u} = 0, \tag{3}$$

$$\rho_f \frac{\partial \mathbf{u}}{\partial t} = -\nabla p + \eta \nabla^2 \mathbf{u} - \rho_e \nabla \phi. \tag{4}$$

In these expressions, η and ρ_f are respectively the viscosity and the density of the liquid phase, and p is the pressure.

Suppose that the applied electric field is weak; then ϕ can be approximated by a sum of the electric potential in the absence of the applied electric field, or as the equilibrium electric potential ϕ_1 and a perturbed potential ϕ_2 [13]:

$$\phi = \phi_1 + \phi_2. \tag{5}$$

In the absence of bulk fluid motion the concentration of ions follows Boltzmann distribution,

$$n_j = n_{j0} \exp\left(-\frac{z_j e \phi}{k_B T} \right), \tag{6}$$

where n_{j0} is the bulk concentration of ionic species j. Here, we assume that the surface potential is low, and, therefore, the effect of double layer relaxation is negligible [1]. In this case Eq. (6) can be approximated by

$$n_j \cong n_{j0} \left(1 - \frac{z_j e \phi}{k_B T} \right). \tag{7}$$

In the absence of the applied electric field $\phi = \phi_1$, and Eqs. (7) and (2) yield

$$\nabla^{*2} \phi_1^* = (\kappa a)^2 \phi_1^*, \tag{8}$$

where $r^* = r/a$ and $\phi^* = \phi/\zeta_a$, ζ_a is the surface potential, and κ is the reciprocal Debye length defined by

$$\kappa = \left(\sum_{j=1}^{2} \frac{n_{j0} (e z_j)^2}{\varepsilon k_B T} \right)^{1/2}. \tag{9}$$

In the absence of applied electric field ϕ_1 is a function of r only, and Eq. (8) becomes

$$\frac{1}{r^{*2}} \frac{\partial}{\partial r^*} \left(r^{*2} \frac{\partial \phi_1^*}{\partial r^*} \right) = (\kappa a)^2 \phi_1^*. \tag{10}$$

The associate boundary conditions are assumed as

$$\phi_1^* = 1, \quad r^* = 1; \tag{11a}$$

$$\phi_1^* = \zeta_b/\zeta_a = \phi_b^*, \quad r^* = 1/H. \tag{11b}$$

Equations (11a) and (11b) imply respectively that the surface of a particle and that of a cavity remain at constant potentials ζ_a and ζ_b.

Equations (2) and (7) give

$$\nabla^{*2}\phi^* = (\kappa a)^2\phi^*. \tag{12}$$

Substituting Eq. (8) into this expression and neglecting terms involving the product of perturbed terms, we obtain

$$\nabla^{*2}\phi_2^* = 0. \tag{13}$$

Since the problem under consideration is ϕ-symmetric, this equation gives

$$\frac{1}{r^{*2}}\frac{\partial}{\partial r^*}\left(r^{*2}\frac{\partial\phi_2^*}{\partial r^*}\right) + \frac{1}{r^{*2}\sin\Theta}\frac{\partial}{\partial\Theta}\left(\sin\Theta\frac{\partial\phi_2^*}{\partial\Theta}\right) = 0. \tag{14}$$

The boundary conditions associated with this expression are assumed as

$$\frac{\partial\phi_2^*}{\partial r^*} = 0, \quad r^* = 1; \tag{15a}$$

$$\frac{\partial\phi_2^*}{\partial r^*} = -E_z^* e^{-i\omega t}\cos\Theta, \quad r^* = 1/H, \tag{15b}$$

where $E_z^* = E_z a/\zeta_a$. Equation (15a) implies that the particle surface is impenetrable to ions, and Eq. (15b) states that the direction of the electric field on the cavity surface is consistent with that of the applied electric field.

The method of separation of variables is applicable to the present problem. Let $\phi_2^* = (\Phi_2^*\cos\Theta)e^{-i\omega t}$. Then Eq. (14) yields

$$\frac{1}{r^{*2}}\frac{\partial}{\partial r^*}\left(r^{*2}\frac{\partial\Phi_2^*}{\partial r^*}\right) - \frac{2\Phi_2^*}{r^{*2}} = 0. \tag{16}$$

The corresponding boundary conditions, Eqs. (15a) and (15b), reduce to

$$\frac{\partial\Phi_2^*}{\partial r^*} = 0, \quad r^* = 1; \tag{17a}$$

$$\frac{\partial\Phi_2^*}{\partial r^*} = -E_z^*, \quad r^* = 1/H. \tag{17b}$$

Equation (4) can be simplified by adopting a stream function representation [14]. If we let ψ be the stream function, then the r and Θ components of $\mathbf{v}$, v_r, and v_θ can be expressed as

$$v_r = -\frac{1}{r^2\sin\Theta}\frac{\partial\psi}{\partial\Theta}, \tag{18}$$

$$v_\theta = \frac{1}{r\sin\Theta}\frac{\partial\psi}{\partial r}. \tag{19}$$

Letting $\mathbf{u} = \mathbf{v}e^{-i\omega t}$ in Eq. (4), and rewriting the resultant expression in terms of ψ, we obtain

$$E^{*4}\psi^* + i\omega^* E^{*2}\psi^* = -(\kappa a)^2\frac{\partial\phi_1^*}{\partial r^*}\frac{\partial\phi_2^*}{\partial\Theta}\sin\Theta, \tag{20}$$

where $\psi^* = \psi/(\varepsilon\zeta_a^2 a/\eta)$, $E^{*4} = E^{*2}E^{*2}$, $\omega^* = \omega\rho_f a^2/\eta$, and

$$E^{*2} = \frac{\partial^2}{\partial r^{*2}} + \frac{\sin\Theta}{r^{*2}}\frac{\partial}{\partial\Theta}\left(\frac{1}{\sin\Theta}\frac{\partial}{\partial\Theta}\right). \tag{21}$$

ω^* represents the scaled frequency of the applied electric field, which is related to the characteristic length δ defined by Landau and Lifshitz [15] for the decay of velocity and pressure in a dynamic spherical system. δ is also known as the penetration depth [5] and can be rewritten as $\delta = (2\eta/\omega\rho_0)^{1/2}$, with ρ_0 being the concentration of electrolyte in the absence of the applied electric field and the charged particle. We have $a/\delta = (\omega^*/2)^{1/2}$. The boundary conditions associated with Eq. (20) are

$$v_r^* = U^* e^{-i\omega t}\cos\Theta, \quad r^* = 1; \tag{22a}$$

$$v_\theta^* = U^* e^{-i\omega t}\sin\Theta, \quad r^* = 1; \tag{22b}$$

$$v_r^* = 0, \quad r^* = 1/H; \tag{22c}$$

$$v_\theta^* = 0, \quad r^* = 1/H. \tag{22d}$$

Equations (22a) and (22b) imply that the velocity on a particle surface is $\mathbf{U}$. Equations (22c) and (22d) state the nonslip condition on the cavity surface. Note that both ψ and $\mathbf{U}$ are complex. For convenience, we let

$$\psi^* = (\psi_R + i\psi_I)e^{-i\omega t}\sin^2\Theta, \tag{23}$$

$$U^* = U_R + iU_I. \tag{24}$$

In these expressions, ψ_R, ψ_I, U_R, and U_I are all real. Substituting Eqs. (23) and (24) into Eq. (20) give the real and the imaginary parts of the resultant expression:

$$\left[\frac{d^2}{dr^{*2}} - \frac{2}{r^{*2}}\right]^2\psi_R = \frac{\omega\rho_f a^2}{\eta}\left[\frac{d^2}{dr^{*2}} - \frac{2}{r^{*2}}\right]\psi_I + (\kappa a)^2\frac{\partial\phi_1^*}{\partial r^*}\Phi_2^*, \tag{25}$$

$$\left[\frac{d^2}{dr^{*2}} - \frac{2}{r^{*2}}\right]^2\psi_I = -\frac{\omega\rho_f a^2}{\eta}\left[\frac{d^2}{dr^{*2}} - \frac{2}{r^{*2}}\right]\psi_R. \tag{26}$$

The associated boundary conditions become

$$\psi_R = -\frac{1}{2}U_R r^{*2} \quad \text{and} \quad \frac{d\psi_R}{dr^*} = -U_R r^*, \quad r^* = 1; \tag{27a}$$

$$\psi_R = 0 \quad \text{and} \quad \frac{d\psi_R}{dr^*} = 0, \quad r^* = 1/H; \tag{27b}$$

$$\psi_I = -\frac{1}{2}U_I r^{*2} \quad \text{and} \quad \frac{d\psi_I}{dr^*} = -U_I r^*, \quad r^* = 1; \tag{27c}$$

$$\psi_I = 0 \quad \text{and} \quad \frac{d\psi_I}{dr^*} = 0, \quad r^* = 1/H. \tag{27d}$$

The force exerted on a particle includes the hydrodynamic drag force F_h and the electric force F_e. Therefore we have

$$F_h + F_e = \frac{4}{3}\pi a^3(\rho_p - \rho_f)\frac{du}{dt}, \tag{28}$$

where ρ_p is the density of the particle. Note that the term $-(4/3)\pi a^3\rho_f\,du/dt$ on the right-hand side of this expression arises from the fact that as the particle moves back and forth in the alternating electric field, no vacuum is left in its water, since the liquid phase is incompressible. This implies that an equivalent amount of liquid in volume has to move in the opposite direction to that of the particle, resulting in an equivalent inertial term in a typical force balance equation. F_h can be expressed as [14]

$$F_h = \eta\pi \int_0^{\pi} \left(r^4 \sin^3 \Theta \frac{\partial}{\partial r} \frac{E^2\psi}{r^2 \sin^2 \Theta} \right)_{r=a} d\Theta - \pi \int_0^{\pi} \left(r^2 \sin^2 \Theta \rho_e \frac{\partial \phi}{\partial \Theta} \right)_{r=a} d\Theta. \tag{29}$$

Substituting Eqs. (5), (7), and (23) into this expression yields

$$F_h = \frac{4}{3}\pi\varepsilon\varsigma_a^2 \times \left(r^{*4} \frac{\partial}{\partial r^*} \left(\frac{1}{r^{*2}} \left(\frac{d}{dr^{*2}} - \frac{2}{r^{*2}} \right) (\psi_R + i\psi_I) \right) \right)_{r^*=1} - \frac{4}{3}\pi\varepsilon\varsigma_a^2 (\kappa a)^2 \left(\phi_1^* \Phi_2^* \right)_{r^*=1}. \tag{30}$$

F_e can be evaluated by

$$F_e = \iint \sigma(-\nabla\phi)\, dA, \tag{31}$$

where σ is the charge density on the particle surface. It can be shown that [10]

$$F_e = \frac{8}{3}\pi\varepsilon\varsigma_a^2 \left(\frac{\partial \phi_1^*}{\partial r^*} \right)_{r^*=1} \left(\Phi_2^* \right)_{r^*=1}. \tag{32}$$

For convenience, the problem under consideration is decomposed into two subproblems [13]. In the first problem a particle moves with velocity $U = (U_R + iU_I)e^{-i\omega t}$ in the absence of the applied electric field, and in the second one an electric field $E_z e^{-i\omega t}$ is applied but the particle remains fixed. The sum of the forces in these two problems, F_1 and F_2, is the same as that expressed in Eq. (28); that is, $F_1 + F_2 = F_h + F_e$. In the first problem, the force required to maintain the movement of the particle is proportional to its velocity, U [3]; that is,

$$F_1 = \alpha(U_R + iU_I)e^{-i\omega t}. \tag{33}$$

Similarly, the force experienced by the particle in the second problem is proportional to the strength of the applied electric field; that is,

$$F_2 = \beta E_z e^{-i\omega t}. \tag{34}$$

α and β in Eqs. (33) and (34) can be complex numbers. Substituting Eqs. (33) and (34) into Eq. (28) yields

$$|\mu| = \frac{|\mathbf{U}|}{|\mathbf{E}|} = \left| -\beta \Big/ \left(\alpha + \frac{i\omega\rho_f a^2}{\eta} \frac{\rho_p - \rho_f}{\rho_f} \right) \right|. \tag{35}$$

The pseudo-spectral method used by Lee et al. [10] is adopted for the resolution of the governing equations subject to the associated boundary conditions.

3. Results and discussion

The behaviors of the mobility and the phase angle θ of the electrophoretic phenomenon under consideration are examined through numerical simulation. For convenience, the scaled mobility μ^*, which is scaled by the mobility evaluated by Smoluchowski's formula for the case of an isolated particle [16], $\mu^* = \mu/(\varepsilon\zeta_a/\eta)$, is used. The phase angle is defined by $\theta = \tan^{-1}(\mu_c/\mu_R)$, where μ_c and μ_R are respectively the imaginary and the real parts of the mobility. A negative θ implies that the electrophoretic velocity leads the applied electric field, and a positive θ implies a phase lag. Three cases are considered: (i) a positively charged particle in an uncharged cavity, (ii) a positively charged particle in a positively charged cavity, and (iii) a positively charged particle in a negatively charged cavity.

Zydney [7] considered the case where an uncharged particle is placed in a positively charged cavity and a static electric field is applied. He concluded that if κa is small (thick double layer), the effect of the cavity on a particle arises mainly from the fact that the cavity will induce an amount of charge, which is equal in magnitude but different in sign, on the particle surface. On the other hand, if κa is large, the effect of the cavity on a particle is mainly due to the electroosmotic flow induced near the cavity surface. Since these two effects have opposite influence on the movement of a particle, the behavior of the particle in a medium κa depends on the net result of these two competing effects. These conclusions are useful for the interpretation of our results.

3.1. Particle is positively charged, and cavity is uncharged

Figure 2 shows the variations of the magnitude of the scaled mobility μ^* and the corresponding phase angle θ as a function of the scaled double layer thickness κa at various scaled frequencies of the applied electric field ω^* for the case of a positively charged particle placed in an uncharged cavity. The semianalytical result of Zydney [7] for the case when a static electric field ($\omega^* = 0$) is applied is also shown for comparison. Figure 2a reveals that for a fixed frequency of the applied electric field, μ^* increases with a decrease in double layer thickness. This is because the thicker the double layer surrounding a particle (smaller κa) the greater the resistance arising from the flow field. Note that μ^* approaches a constant value as $\kappa a \to 0$. As $\kappa a \to \infty$, μ^* also approaches a constant value, which is smaller than unity. This is because the presence of the cavity wall has the effect of retarding the movement of a particle, and therefore, the limiting mobility of the particle is smaller than that for the case when it is placed in an infinite fluid. For a fixed double layer thickness, Fig. 2a indicates that μ^* decreases with an increase in the frequency of the applied electric field. This is because the higher the frequency, the shorter the time interval available to accelerate the particle. Apparently, the mobility for the case when a dynamic electric field is

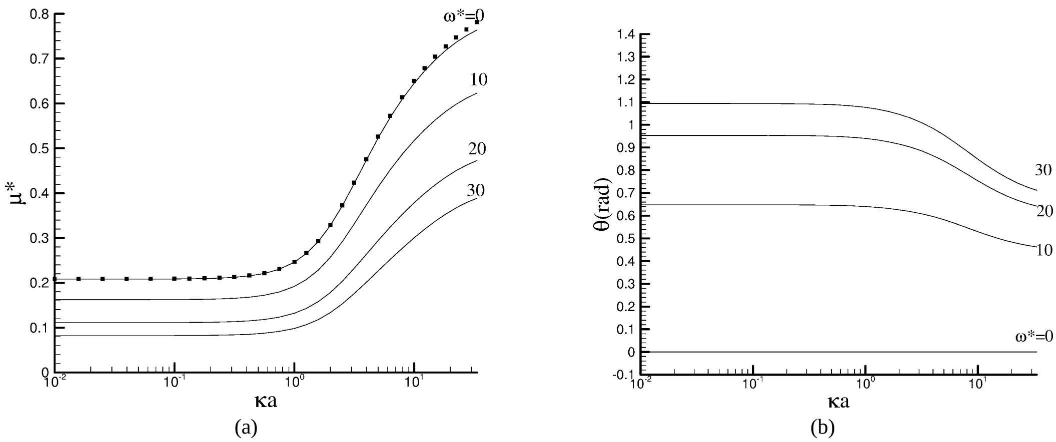

Fig. 2. Variation of (a) the magnitude of the scaled mobility μ^* and (b) the phase angle θ, as a function of double layer thickness κa at various scaled frequencies of applied electric field ω^* for the case of a positively charged particle placed in an uncharged particle with $H = 0.5$. Discrete symbols represent the semianalytical result of Zydney [7] for the case when a static electric field is applied. 1:1 electrolyte; $E_z^* = 1.0$; $U^* = 1.0$.

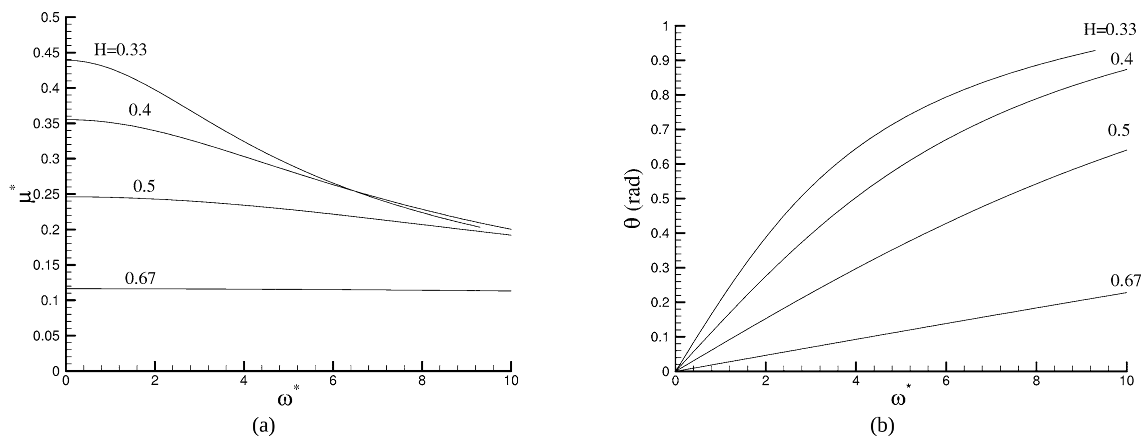

Fig. 3. Variation of (a) the magnitude of the scaled mobility μ^* and (b) the phase angle θ, as a function of scaled frequency of the applied electric field ω^* at various H for the case of a positively charged particle placed in an uncharged cavity with $\kappa a = 1$. 1:1 electrolyte; $E_z^* = 1.0$; $U^* = 1.0$.

applied is smaller than that for the case when a static electric field ($\omega^* = 0$) is applied. Figure 2a also reveals that the larger the κa, the more pronounced the effect of ω^* on μ^*. Figure 2b shows that for a fixed ω^*, the thinner the double layer (larger κa) the less significant the phase lag, and for a fixed double layer thickness, the higher the frequency of the applied electric field the more significant the phase lag. As can be seen in Fig. 2a, the result of Zydney [7] can be recovered as a special case of the present study by letting $\omega^* = 0$.

The effect of the presence of the cavity wall on the electrophoretic behavior of the particle is presented in Fig. 3. Illustrated are the variations of the magnitude of the scaled mobility μ^* and the corresponding phase angle θ as a function of the scaled frequency of the applied electric field ω^* at various H for the case when the particle is positively charged and the cavity is uncharged. According to its definition, H $(= a/b)$ is a measure for the effect of the presence of the cavity wall; the smaller its value the less significant the effect. Figure 3a shows that, for a fixed H, μ^* decreases with ω^*, which is consistent with the result shown in Fig. 2a. However, if H is sufficiently large, μ^* is insensitive to the variation in ω^*. This is because if H is large, the mobility of the particle is confined by the cavity, and the effect of the applied electric field becomes insignificant. In a study of the dynamic mobility of a concentrated colloidal dispersion Ohshima [17] concluded that the effect of the frequency of the applied electric field on the dynamic mobility is significant only if the penetration depth δ $(= (2\eta/\omega\rho_f)^{1/2})$ is smaller than $2(b - a)$. If the radius of the cavity corresponds to that of the liquid shell in the cell model of Ohshima, then in terms of our notation, we have $(\delta/a) = \sqrt{2/\omega^*}$. Applying Ohshima's criterion, we see that the effect of the frequency of the applied electric field becomes important if ω^* exceeds 2.5, 0.9, 0.3, and 0.2 for the cases when H is 0.67, 0.5, 0.4, and 0.33, respectively. As can be seen from Fig. 3a, our result is consistent with that of Ohshima.

3.2. Both particle and cavity are positively charged

Figure 4 presents the variations of the magnitude of the scaled mobility μ^* and the corresponding phase angle θ as a function of κa at various scaled frequencies of the applied

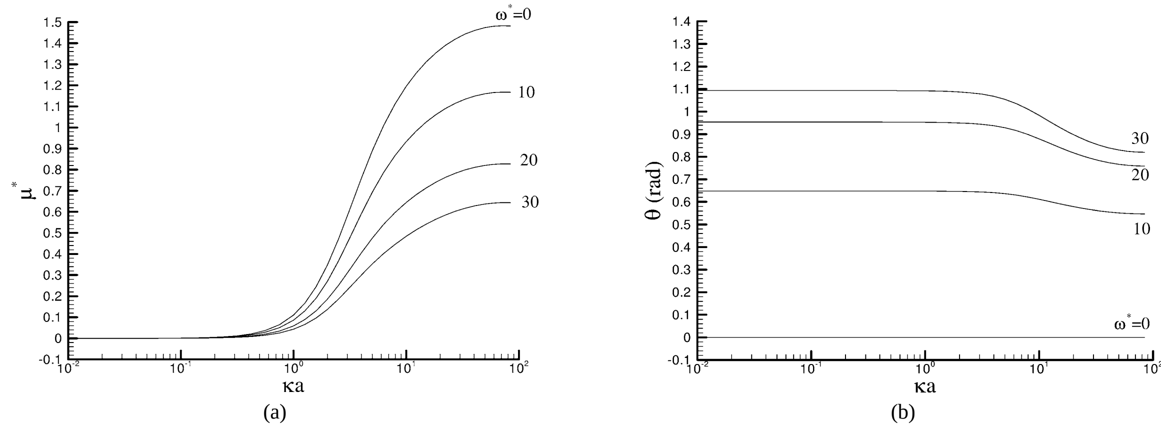

Fig. 4. Variation of (a) the magnitude of the scaled mobility μ^* and (b) the phase angle θ, as a function of double layer thickness κa at various scaled frequencies of applied electric field ω^* for the case when both particle and cavity are positively charged with $H = 0.5$ and $\phi_b^* = 1$. 1:1 electrolyte; $E_z^* = 1.0$; $U^* = 1.0$.

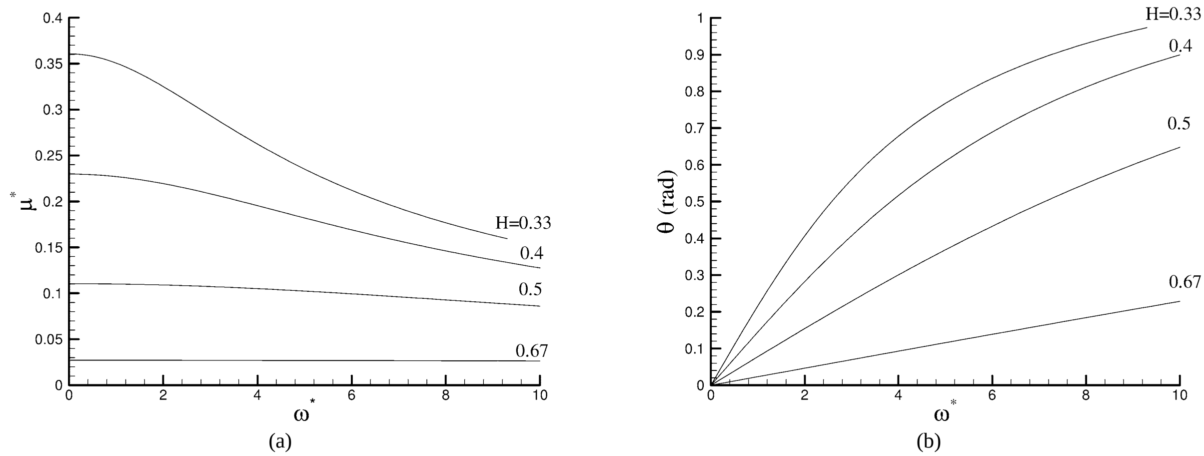

Fig. 5. Variation of (a) the magnitude of the scaled mobility μ^* and (b) the phase angle θ, as a function of scaled frequency of applied electric field ω^* at various H for the case when both particle and cavity are positively charged with $\kappa a = 1$ and $\phi_b^* = 1$. 1:1 electrolyte; $E_z^* = 1.0$; $U^* = 1.0$.

electric field ω^* for the case whose both the particle and the cavity are positively charged, and those at various H are shown in Fig. 5. The qualitative behaviors of the curves in Figs. 4 and 5 are similar to those presented in Figs. 2 and 3, respectively. A comparison between Figs. 2 and 4 reveals that if κa is sufficiently large, μ^* for the case when both particle and cavity are positively charged is larger than that for the case when the particle is positively charged and the cavity is uncharged. This is because if the cavity is positively charged, a double layer, which is richer in anions, is formed near it. Since the direction of the electroosmotic flow inside this double layer is the same as that of the applied electric field, its effect on the mobility of the particle is positive, and the mobility is larger than that when the cavity is uncharged [7]. Figures 2 and 4 also show that the phage lag for the case when the cavity is positively charged is slightly larger than that for the case when it is uncharged. Figure 4a indicates that, unlike the result shown in Fig. 2a, the magnitude of the mobility vanishes as $\kappa a \to 0$. This is because the presence of the cavity has the effect of inducing negative charge on the particle surface, which tends to move the particle in a direction that is opposite to that if the particle is positively charged. As in the case of Fig. 2a, the larger the ω^* the smaller the μ^*, and the larger the κa, the more pronounced the effect of ω^* on μ^*. This is because the higher the frequency of the applied electric field the more significant the phase lag, as presented in Fig. 4b. Due to the presence of the phase lag, the direction of the electroosmotic flow mentioned previously can be different from that of the movement of the particle, and therefore, its positive effect at a higher frequency can be less significant than that for the case of a lower frequency.

3.3. Particle is positively charged and cavity is negatively charged

Figure 6 shows the variations of the magnitude of the scaled mobility μ^* and the corresponding phase angle θ as a function of κa at various scaled frequencies of the applied electric field ω^* for the case when the particle is positively charged and the cavity is negatively charged, and those at various H are shown in Fig. 7. Figure 6a reveals that μ^* decreases with an increase in κa, passing through a local minimum in a medium κa, and then increases with

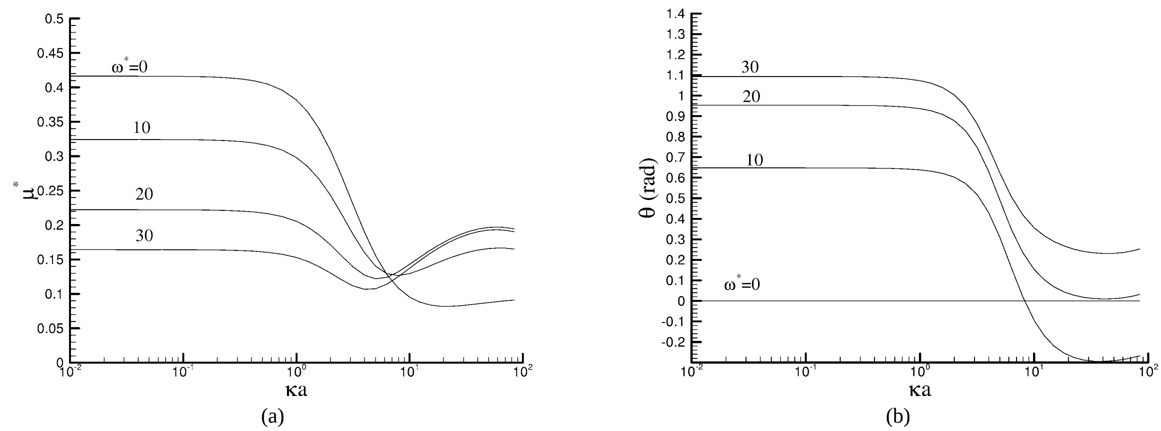

Fig. 6. Variation of (a) the magnitude of the scaled mobility μ^* and (b) the phase angle θ, as a function of double layer thickness κa at various scaled frequencies of the applied electric field ω^* for the case of a positively charged particle placed in a negatively charged cavity with $H = 0.5$ and $\phi_b^* = -1$. 1:1 electrolyte; $E_z^* = 1.0$; $U^* = 1.0$.

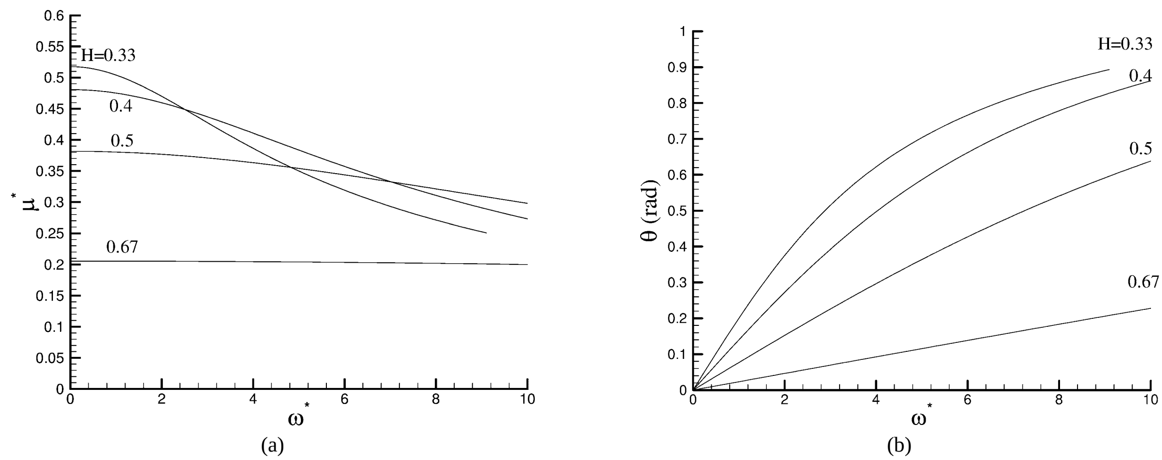

Fig. 7. Variation of (a) the magnitude of the scaled mobility μ^* and (b) the phase angle θ, as a function of scaled frequency of applied electric field ω^* at various H for the case of a positively charged particle placed in a negatively charged cavity with $\kappa a = 1$ and $\phi_b^* = -1$. 1:1 electrolyte; $E_z^* = 1.0$; $U^* = 1.0$.

a further increase in κa. This is because as κa is getting large, the effect of the electroosmotic flow near the cavity surface, which has a negative effect on particle movement, comes into play, and, therefore μ^* decreases accordingly. It is interesting to note in Fig. 6a that if κa is small, μ^* decreases with an increase in ω^*, as in the cases of Figs. 2a and 4a, but the opposite is true if κa is large. The later is because the larger the κa, the more significant the effect of ω^* on μ^*, as suggested by Figs. 2a and 4a. The local minimum shown in Fig. 6a may arise from a combined effect of the presence of the cavity and the signs of the charge on the surfaces of the particle and the cavity. A local minimum in μ^* as κa varies was also observed by Lee et al. [10] for the case of a static applied electric field. Note that the local minimum shown in Fig. 6a for the case $\omega^* = 0$ was not observed by Zydney [7]. Figure 6b reveals that if the frequency of the applied electric field is low and the double layer is thin, a phase lead in the electrophoretic mobility may be observed. A comparison between Figs. 2a and 6a suggests that if κa is small, the magnitude of the mobility of the latter is twice that of the former. This is because the negatively charged cavity will induce a positive charge on the particle surface. Figures 2, 4, and 6 reveal that the effect of the frequency of the applied electric field on the electrophoretic behavior of the particle for the case when the cavity is negatively charged is more pronounced than that for the case when it is positively charged or uncharged.

4. Conclusion

In summary, the dynamic electrophoretic behavior of a positively charged sphere in a spherical cavity is investigated for the case of low surface potential. The results of numerical simulation can be summarized as follows. If the cavity is uncharged, the magnitude of the mobility of the particle increases with a decrease in the thickness of the double layer surrounding the particle. The magnitude of the mobility is found to approach a constant value for the cases when either the double layer is infinitely thin or it is infinitely thick. We show that the mobility decreases with an increase in the frequency of the applied electric field, and this effect is pronounced if the double layer is thin. The phase lag of the mobility decreases with a decrease both in double layer thickness and in frequency. The effect of the frequency on the mobility becomes inappreciable if the particle is sufficiently close to the cavity.

The qualitative behaviors of the electrophoretic mobility for the case when the cavity is positively charged are similar to that for the case when it is uncharged. If the double layer surrounding a particle is thin, the magnitude of mobility for the case when the cavity is positively charged is larger than that for the case when it is uncharged. The phage lag for the case when the cavity is positively charged is slightly larger than that for the case when it is uncharged. Unlike the case when the cavity is uncharged, the magnitude of the mobility vanishes as the double layer becomes infinitely thick.

If the cavity is negatively charged, the magnitude of the mobility has a local minimum as the thickness of the double layer varies. If the double layer is thick, the magnitude of the mobility decreases with an increase in the frequency, but the opposite is true if it is thin. A phase lead in the mobility may be observed if the frequency is low and the double layer in thin. If the double layer is infinitely thick, the magnitude of the mobility for the case when the cavity is negatively charged is twice that for the case when it is uncharged. The effect of frequency on the electrophoretic behavior of the particle for the case when the cavity is negatively charged is more pronounced than that for the cases when it is either positively charged or uncharged.

Acknowledgment

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

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