Colloid Vibration Potential in a Concentrated Suspension of Spherical Colloidal Particles

Hiroyuki Ohshima[*,1] and Andrei S. Dukhin[†]

Faculty of Pharmaceutical Sciences and Institute of Colloid and Interface Science, Science University of Tokyo, 12 Ichigaya Funagawara-machi, Shinjuku-ku, Tokyo 162-0826, Japan; and †Dispersion Technology Inc., 3 Hillside Avenue, Mount Kisco, New York 10549

A relation between the dynamic electrophoretic mobility of spherical colloidal particles in a concentrated suspension and the colloid vibration potential (CVP) generated in the suspension by a sound wave is obtained from the analogy with the corresponding Onsager relation between electrophoretic mobility and sedimentation potential in concentrated suspensions previously derived on the basis of Kuwabara's cell model. The obtained expression for CVP is applicable to the case where the particle zeta potential is low, the particle relative permittivity is very small, and the overlapping of the electrical double layers of adjacent particles is negligible. It is found that CVP shows much stronger dependence on the particle volume fraction ϕ than predicted from the ϕ dependence of the dynamic electrophoretic mobility. It is also suggested that the same relation holds between the electrokinetic sonic amplitude of a concentrated suspension of spherical colloidal particles and the dynamic electrophoretic mobility. © 1999 Academic Press

Key Words: colloid vibration potential; dynamic electrophoretic mobility; concentrated suspension; spherical particle; cell model.

1. INTRODUCTION

When a suspension of charged colloidal particles is irradiated with a sound wave, a macroscopic electric field is generated in the suspension. This field is called the colloid vibration potential (CVP). The mechanism of the generation of CVP is essentially the same as that for the sedimentation potential in a suspension of charged colloidal particles in a gravitational field (see, e.g., Ref. (1)). For a dilute suspension it has been shown by Enderby (2) that the CVP in a suspension of spherical colloidal particles in an applied sonic field of frequency ω is related to the dynamic electrophoretic mobility μ_D of the particle by

$$\text{CVP} = \frac{\phi(\rho_p - \rho_0)}{\rho_0 K^\infty} \mu_D \nabla p, \qquad [1]$$

where ∇p is the pressure gradient due to the sound wave, ϕ is

[1] To whom correspondence should be addressed.

the particle volume fraction, ρ_p is the mass density of the particle, ρ_0 is the mass density of the electrolyte solution, and K^∞ is the electrical conductivity of the electrolyte solution in the absence of the particles. An approximate expression for the dynamic mobility of a spherical particle of radius a has been derived by O'Brien (3), which is, for the case where $\kappa a \gg 1$ (where κ is the Debye–Hückel parameter) and the dynamic relaxation effect is neglected,

$$\mu_D = \frac{\varepsilon_r \varepsilon_0 \zeta}{\eta} \frac{1 - i\gamma a}{H(a) - \Gamma}, \qquad [2]$$

with

$$\gamma = \sqrt{\frac{i\omega\rho_0}{\eta}} = (i + 1)\sqrt{\frac{\omega\rho_0}{2\eta}}, \qquad [3]$$

$$\Gamma = \frac{2(\gamma a)^2(\rho_p - \rho_0)}{9\rho_0}, \qquad [4]$$

$$H(a) = 1 - i\gamma a - \frac{(\gamma a)^2}{3}, \qquad [5]$$

where ε_r is the relative permittivity of the solution, ε_0 is the permittivity of a vacuum, η is the viscosity, and ζ is the zeta potential of the particle.

Equation [1], which is correct to the first order of ϕ, is applicable only for dilute suspensions. The purpose of the present paper is to generalize Eq. [1] to cover the case of concentrated suspensions on the basis of Kuwabara's cell model (4).

2. KUWABARA'S CELL MODEL

For concentrated suspensions, the hydrodynamic and electrostatic interactions between the particles must be taken into account. One useful and simple method is to employ Kuwabara's cell model (4) (see Fig. 1 of the preceding article on p. 444). This model assumes that each sphere of radius a is surrounded by a concentric spherical shell of an electrolyte

solution having an outer radius of b such that the particle/cell volume ratio in the unit cell is equal to the particle volume fraction ϕ throughout the entire suspension, viz.,

$$\phi = (a/b)^3 \qquad [6]$$

and that the fluid vorticity is zero at the outer surface of the unit cell. Levine and Neale (5) proposed a theory of the static electrophoretic mobility of spherical particles in concentrated suspensions on the basis of Kuwabara's cell model and demonstrated that in the limit of $\kappa a \rightarrow \infty$ Kuwabara's cell model correctly gives Smoluchowski's mobility formula,

$$\mu_s = \frac{\varepsilon_r \varepsilon_0 \zeta}{\eta}. \qquad [7]$$

Also Ohshima (6) showed that the electrical conductivity K^* of a concentrated suspension of spherical particles calculated on the basis of Kuwabara's cell model has the correct behaviors in the following two limiting cases: $\zeta = 0$ (uncharged particles) and $\kappa a \rightarrow \infty$ (infinitesimally thin electrical double layers around the particles). That is, Kuwabara's cell model yields Maxwell's formula (7) in these limiting cases,

$$\frac{K^*}{K^\infty} = \frac{1 - \phi}{1 + \phi/2}, \quad (\zeta = 0) \qquad [8]$$

and

$$\frac{K^*}{K^\infty} = \frac{1 - \phi}{1 + \phi/2}, \quad (\kappa a \rightarrow \infty), \qquad [9]$$

where K^∞ is the conductivity of the electrolyte solution in the absence of the particles. These correct behaviors exhibited by Kuwabara's cell model imply that this model is a good approximation for concentrated suspensions. Also note that Kuwabara's cell model assumes a uniform three-dimensional distribution of particles. As shown by Kang and Sangani (8), however, the exact particle distribution plays a minor role unless the double layers around the particles are very thick.

3. ANALOGY BETWEEN CVP AND SEDIMENTATION POTENTIAL

Equation [1] is similar to the following well-known relation between the sedimentation potential $\mathbf{E}_{sed}$ in a dilute suspension of colloidal particles and the static electrophoretic mobility μ of the particle, viz.

$$\mathbf{E}_{SED} = -\frac{\phi(\rho_p - \rho_0)}{K^\infty} \mu \mathbf{g}, \qquad [10]$$

where $\mathbf{g}$ is the gravity. This relation was originally derived by de Groot et al. (9) on the basis of irreversible thermodynamics and later a direct proof of Eq. [10] was given by Ohshima et al. (10). The similarity between Eqs. [1] and [10], which are both Onsager's reciprocal relations, results from the analogy between sedimentation potential in a gravitational field and colloid vibration potential in a sonic field. In the limit of large κa, the static mobility μ is given by Smoluchowski's formula [7].

4. SEDIMENTATION POTENTIAL IN CONCENTRATED SUSPENSIONS

Levine et al. (11) employed Kuwabara's cell model to derive the following expression for the sedimentation potential $\mathbf{E}_{sed}$ in a concentrated suspension of spherical particles of radius a with zeta potential ζ, which is correct to the first order of ζ,

$$\mathbf{E}_{SED} = -\frac{\varepsilon_r \varepsilon_0 \zeta}{\eta} \frac{\phi(\rho_p - \rho_0)}{K^\infty} \frac{\gamma(\kappa a, \phi)}{\Omega(\phi)} \mathbf{g}, \qquad [11]$$

where $\Omega(\phi)$ is defined by

$$\Omega(\phi) = (1 + \phi - 9\phi^{1/3}/5 - \phi^2/5)^{-1} \qquad [12]$$

and $\gamma(\kappa a, \phi)$ is a very complicated function and given in Ref. (11). Equation [11] is applicable for low zeta potentials and nonoverlapping of electrical double layers of adjacent particles. Recently Ohshima (12) has found that $\gamma(\kappa a, \phi)$ can be simply expressed in terms of the static electrophoretic mobility $\mu(\kappa a, \phi)$ in concentrated suspensions as

$$\gamma(\kappa a, \phi) = \frac{(1 - \phi)\Omega(\phi)}{(1 + \phi/2)} \frac{\mu(\kappa a, \phi)}{(\varepsilon_r \varepsilon_0 \zeta/\eta)} \qquad [13]$$

and thus Eq. [11] can be rewritten as

$$\mathbf{E}_{SED} = -\frac{\phi(1 - \phi)}{(1 + \phi/2)} \frac{(\rho_p - \rho_0)}{K^\infty} \mu(\kappa a, \phi)\mathbf{g}. \qquad [14]$$

Here $\mu(\kappa a, \phi)$ is the static electrophoretic mobility of spherical colloidal particles of radius a in a concentrated suspension derived by Levine and Neale (5) on the basis of Kuwabara's cell model and a simple accurate approximate expression for $\mu(\kappa a, \phi)$ has recently been obtained by Ohshima (13).

5. CVP IN CONCENTRATED SUSPENSIONS

By analogy between the sedimentation potential and CVP, the following formula for the CVP in a concentrated suspension of spherical colloidal particles of radius a with zeta potential ζ immediately results:
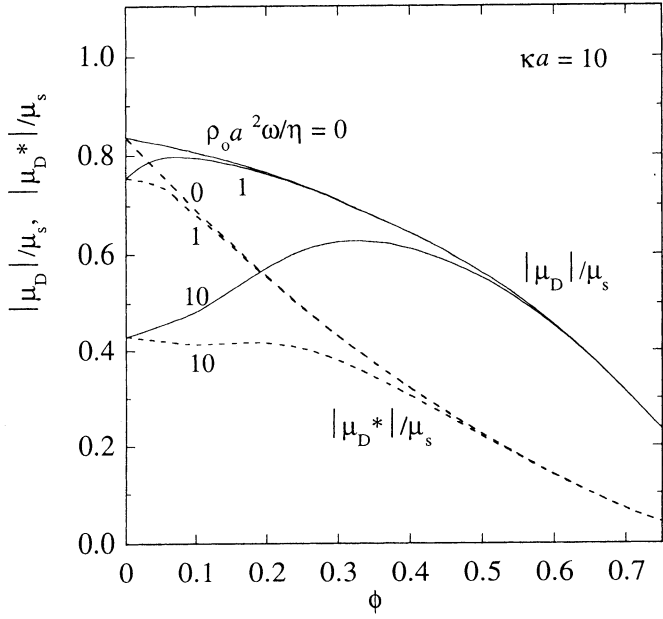
FIG. 1. Magnitude of the dynamic electrophoretic mobility $\mu_D(\kappa a, \phi)$ and $\mu_D^*(\kappa a, \phi)$, both scaled by μ_s (where $\mu_s = \varepsilon_r\varepsilon_0\zeta/\eta$ is Smoluchowski's mobility) as a function of the particle volume fraction ϕ for several values of $\rho_0 a^2\omega/\eta(=|\gamma^2|a^2)$ at $(\rho_p - \rho_0)/\rho_0 = 0.1$ and $\kappa a = 10$. Solid lines represent $|\mu_D(\kappa a, \phi)|/\mu_s$ and dotted lines $|\mu_D^*(\kappa a, \phi)|/\mu_s$.

$$\text{CVP} = \frac{\phi(1 - \phi)}{(1 + \phi/2)}\frac{(\rho_p - \rho_0)}{\rho_0 K^\infty}\mu_D(\kappa a, \phi)\nabla p. \quad [15]$$

Here $\mu_D(\kappa a, \phi)$ is the dynamic electrophoretic mobility of spherical colloidal particles of radius a with zeta potential ζ in concentrated suspensions. Ohshima (14, 15) has derived the following accurate expression for $\mu_D(\kappa a, \phi)$:

$$\mu_D(\kappa a, \phi) = \frac{\varepsilon_r\varepsilon_0\zeta}{\eta[M(a) - \Gamma]}$$
$$\times \left\{\frac{2}{3}\left[1 + \frac{1}{2(1 + \delta/\kappa a)^3}\right]S_1 + S_2\right\}, \quad [16]$$

where

$$M(a) = \frac{H(a) + i\gamma a(1 - R)}{1 - \phi + [3\phi/(\gamma a)^2](1 - i\gamma aR)}, \quad [17]$$

$$S_1 = \frac{1}{1 - \phi}\left[-\frac{(\kappa a)^2}{3\phi^{2/3}P}\right.$$
$$\left.+ \frac{\gamma^2(1 + \kappa aQ) + \kappa^2(1 - i\gamma aR)}{(\gamma^2 + \kappa^2)\{1 - \phi + [3\phi/(\gamma a)^2](1 - i\gamma aR)\}}\right], \quad [18]$$

$$S_2 = \frac{2(1 + \phi/2)(\kappa a)^2}{9\phi^{2/3}(1 - \phi)P}, \quad [19]$$

$$P = \cosh[\kappa(b - a)] - \frac{1}{\kappa b}\sinh[\kappa(b - a)], \quad [20]$$

$$Q = \frac{1 - \kappa b \cdot \tanh[\kappa(b - a)]}{\tanh[\kappa(b - a)] - \kappa b}, \quad [21]$$

$$R = \frac{(1 + i\gamma b)e^{-i\gamma(b-a)} + (1 - i\gamma b)e^{i\gamma(b-a)}}{(1 + i\gamma b)e^{-i\gamma(b-a)} - (1 - i\gamma b)e^{i\gamma(b-a)}}, \quad [22]$$

$$\delta = \frac{2.5}{1 + 2\exp(-\kappa a)}, \quad [23]$$

where γ, Γ, and $H(a)$ are defined by Eqs. [3]–[5], and $b = a\phi^{-1/3}$ (Eq. [6]). Equation [15] is applicable when the zeta potential is low, the particle permittivity is very small, and the overlapping of the double layers of adjacent particles is negligible. Note also that in the approximation of nonoverlapping double layers $S_2(\kappa a, \phi)$ in Eq. [16] can be ignored. In the limit of $\kappa a \to \infty$, in particular, Eq. [16] reduces to

$$\mu_D(\infty, \phi) = \frac{\varepsilon_r\varepsilon_0\zeta}{\eta(1 - \phi)}$$
$$\times \frac{1 - i\gamma aR}{H(a) + i\gamma a(1 - R) - \Gamma\{1 - \phi}{+ [3\phi/(\gamma a)^2](1 - i\gamma aR)\}} \quad [24]$$
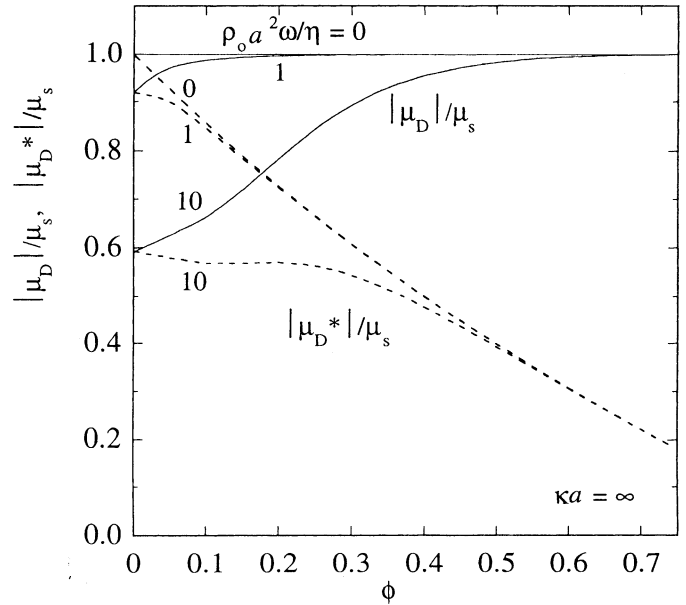

FIG. 2. Same as Fig. 1 but for $\kappa a = \infty$.

which further reduces to O'Brien's mobility formula [2] as $\phi \to 0$.

Equation [15], which is the required expression for the CVP in concentrated suspensions, is the generalization of Eq. [1] to cover the case of concentrated suspensions.

6. RESULTS AND DISCUSSION

We have derived Eq. [15] for the CVP in concentrated suspensions of spherical colloidal particles on the basis of the observation that Onsager's relation between CVP and dynamic electrophoresis is the same as that between sedimentation potential and static electrophoresis. It must be stressed that Onsager's relations for concentrated suspensions (Eqs. [14] and [15]) differ from those for dilute suspensions (Eqs. [1] and [10]) in that Eqs. [14] and [15] have a factor $(1 - \phi)/(1 + \phi/2)$. It is interesting to note that this factor coincides with the electrical conductivity ratio K^*/K^∞ given by Maxwell's relation (Eqs. [8] and [9]). Due to the presence of the factor $(1 - \phi)/(1 + \phi/2)$, the CVP depends more strongly on ϕ than predicted from the ϕ dependence of $\mu_D(\kappa a, \phi)$. In order to see this more clearly, we introduce

$$\mu_D^*(\kappa a, \phi) = \frac{1 - \phi}{1 + \phi/2} \mu_D(\kappa a, \phi), \qquad [25]$$

which is related to CVP by

$$CVP = \frac{\phi(1 - \phi)}{(1 + \phi/2)} \frac{(\rho_p - \rho_0)}{\rho_0 K^\infty} \mu_D(\kappa a, \phi) \nabla p$$

$$= \phi \frac{(\rho_p - \rho_0)}{\rho_0 K^\infty} \mu_D^*(\kappa a, \phi) \nabla p. \qquad [26]$$

We compare the magnitudes of $\mu_D(\kappa a, \phi)$ and $\mu_D^*(\kappa a, \phi)$ for $\kappa a = 10$ and ∞ in Figs. 1 and 2, where calculation was made with the help of Eqs. [16] ($\kappa a = 10$) and [24] ($\kappa a = \infty$) for several values of $\rho_0 a^2 \omega/\eta(=|\gamma^2|a^2)$ at $(\rho_p - \rho_0)/\rho_0 = 0.1$. We see that $|\mu_D^*(\kappa a, \phi)|$ shows much stronger dependence on ϕ than $|\mu_D(\kappa a, \phi)|$. That is, CVP exhibits much stronger depen-

dence on ϕ than predicted from the ϕ dependence of the dynamic electrophoretic mobility $\mu_D(\kappa a, \phi)$.

The results obtained in this paper can also be applied to other electroacoustic phenomena. When an oscillating electric field $\mathbf{E} \exp(-i\omega t)$ is applied to a suspension of charged spherical colloidal particles, a macroscopic sound wave is generated in the suspension. O'Brien (3) showed that Onsager's reciprocal relation holds between the oscillating electric field generated by a sound wave and the sound wave generated by an oscillating electric field. It is thus suggested that the amplitude of this sound wave, which is called electrokinetic sonic amplitude (ESA), can be expressed as

$$ESA = B \frac{\phi(1 - \phi)}{(1 + \phi/2)} (\rho_p - \rho_0)\mu_D(\kappa a, \phi) E$$

$$= B\phi(\rho_p - \rho_0)\mu_D^*(\kappa a, \phi) E, \qquad [27]$$

where B is the instrument factor and $E = |\mathbf{E}|$.

REFERENCES

1. Takeda, S., "Electrical Phenomena at Interfaces, 2nd Edition" (H. Ohshima and K. Furusawa, Eds.), Chap. 13, Sec. 1, Marcel Dekker, New York, 1998.
2. Enderby, J. A., *Proc. Phys. Soc. A* **207**, 329 (1951).
3. O'Brien, R. W., *J. Fluid Mech.* **190**, 71 (1988).
4. Kuwabara, S., *J. Phys. Soc. Japan* **14**, 527 (1959).
5. Levine, S., and Neale, G. H., *J. Colloid Interface Sci.* **47**, 520 (1974).
6. Ohshima, H., *J. Colloid Interface Sci.* **212**, 443 (1999).
7. Maxwell, J. C., "A Treatise on Electricity and Magnetism," Vol. 1, Art. 313. Dover, New York, 1954.
8. Kang, S-Y., and Sangani, A. S., *J. Colloid Interface Sci.* **165**, 195 (1994).
9. de Groot, S. R., Mazur, P., and Overbeek, J. Th. G., *J. Chem. Phys.* **20**, 1825 (1952).
10. Ohshima, H., Healy, T. W., White, L. R., and O'Brien, R. W., *J. Chem. Soc. Faraday Trans. 2* **80**, 1299 (1984).
11. Levine, S., Neale, G. H., and Epstein, N., *J. Colloid Interface Sci.* **57**, 424 (1976).
12. Ohshima, H., *J. Colloid Interface Sci.* **208**, 295 (1998).
13. Ohshima, H., *J. Colloid Interface Sci.* **188**, 481 (1997).
14. Ohshima, H., *J. Colloid Interface Sci.* **195**, 137 (1997).
15. Ohshima, H., "Electrical Phenomena at Interfaces, 2nd Edition" (H. Ohshima and K. Furusawa, Eds.), Chap. 2, Marcel Dekker, New York, 1998.