Electrophoresis of a concentrated aqueous dispersion of non-Newtonian drops

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Abstract

The electrophoresis of a concentrated dispersion of non-Newtonian drops in an aqueous medium, which has not been investigated theoretically in the literature, is analyzed under conditions of low zeta potential and weak applied electric field. The results obtained provide a theoretical basis for the characterization of the nature of an emulsion and a microemulsion system. A Carreau fluid, which has wide applications in practice, is chosen for the non-Newtonian drops, and the unit cell model of Kuwabara is adopted to simulate a dispersion. The effects of the key parameters of a dispersion, including its concentration, the shear-thinning nature of the drop fluid, and the thickness of the double layer, on the electrophoretic behavior of a drop are discussed. In general, the more significant the shear-thinning nature of the drop fluid is, the larger the mobility is, and this effect is pronounced as the thickness of the double layer decreases. However, if the double layer is sufficiently thick, this effect becomes negligible. In general, the higher the concentration of drops is, the smaller the mobility is; however, if the double layer is either sufficiently thin or sufficiently thick, this effect becomes unimportant.

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1. Introduction

The stability of a colloidal dispersion is closely related to the charged conditions on the surfaces of the dispersed entities. Because the applications of a colloidal dispersion depend largely on its stability, the estimation of the charged nature of an entity becomes one of the key issues in colloidal science. In practice, this is usually accomplished by electrophoretic measurements. Electrophoresis also plays an important role as a separation method in industrial processes. In the United States, for example, about 4×10^5 BTU of energy is consumed in separation or purification of chemicals [1], and a large fraction of this amount of energy was wasted due to low separation efficiency, which is harmful to

both the economy and the environment. Electrophoresis is one of the potential techniques for improving separation efficiency.

Under conditions of low surface potential and thin double layer, Smoluchowski [2] was able to derive an analytical expression relating the electrophoretic velocity of a rigid, isolated particle in an infinite fluid as a function of its surface potential and the applied electric field. The same problem was investigated by Hückel [3] for the case where the double layer is very thick. Subsequent analyses are ample in the literature; due to the complicated nature of the problem under consideration, however, they are mainly limited to drastically simplified cases [4,5]. The difficulty arises from the fact that the governing equations are coupled, highly nonlinear partial differential equations, and solving these equations analytically under general conditions is almost impossible. In fact, even solving them numerically can be challenging. O'Brien and White [6] proposed us-

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ing a shooting method to solve the electrophoresis of an isolated sphere in an infinite fluid for the case of arbitrary double-layer thickness and arbitrary surface potential; the effect of double-layer polarization was taken into account for the case of a weak applied electric field. In a recent series of studies, Lee and co-workers [7–10] proposed using a pseudo-spectral method [11] to solve the electrophoresis under the influence of a boundary [12]. The performance of the numerical scheme adopted was found to be satisfactory in solving complicated problems that involve arbitrary surface potential, arbitrary double-layer thickness, arbitrary strength of applied electric field, and double-layer polarization. The electrophoresis of nonrigid entities was originated by Craxford et al. [13], who investigated the behavior of a mercury drop. Due to their specific physical nature, which is ideal for model construction, subsequent analyses on nonrigid entities were mainly based on mercury drops [14–17].

Liquid–liquid dispersion, or emulsion, is one of the important classes of colloidal dispersion in practice. Recently, emulsions in which drop size ranged from about 5 to 50 nm [18,19], or microemulsions, have drawn the attention of researchers in various areas. These thermodynamically stable systems have many practical applications, ranging from conventional ones such as detergents and tertiary oil recovery to high-technology ones such as preparation of nanosized particles. The surface of a drop in an emulsion system is usually charged, which arises from the dissociation of the surfactant molecules. This implies that electrophoresis can play a role in describing the physical properties of an emulsion system. A thorough review of the literature reveals that although experimental studies are extensive, relevant theoretical analyses are very limited. In particular, the case when a drop is of non-Newtonian nature has not been investigated. An emulsion system of this nature is often observed in practice. The preparation of polymeric micro- or nanosized particles through polymerization conducted in an emulsion, for example, involves such a system. Compared with the electrophoresis of a rigid dispersion, the electrophoresis of an emulsion is more complicated. This is because in addition to solving the flow field outside an entity, that inside it also needs to be considered. The match of the flow field outside a drop and that inside it can be nontrivial in the numerical treatment of the governing equations of the flow field. The non-Newtonian nature of a drop also adds some difficulty to the solution procedure.

In this study, the electrophoresis of a concentrated aqueous dispersion of non-Newtonian drops is analyzed theoretically. A Carreau fluid, which has wide applications in many areas [20,21], is chosen for the drop fluid, and the unit cell model of Kuwabara [22] is adopted to simulate a dispersion. The electrokinetic equations describing the present boundary-valued problem are solved by a pseudo-spectral method, and the effects of the key parameters of a dispersion on its electrophoretic behavior are discussed.

Fig. 1. Schematic representation of the problem considered. An electric field E is applied to a concentrated spherical dispersion of monodisperse, non-Newtonian drops of radius a , and U is the electrophoretic velocity of drops. The dispersion is simulated by Kuwabara's unit cell model, where a cell comprises a drop and a concentric spherical liquid shell of radius b .

Fig. 2. Coordinates used in mathematical modeling, where (r, θ, ϕ) are the spherical coordinates with origin at the center of a drop.

2. Theory

Referring to Fig. 1, we consider monodisperse, spherical, non-Newtonian drops in an aqueous solution containing $z_1:z_2$ electrolyte, z_1 and z_2 being respectively the valences of cations and anions. Let a be the radius of a drop and $z_2 = -\alpha z_1$. A uniform electric field E is applied, and U is the electrophoretic velocity of drops. Adopting Kuwabara's unit cell model [22], the dispersed system is simulated by a representative cell, which contains a drop and a concentric liquid shell of radius b as shown in Fig. 2. Let $H = a/b$, which measures the concentration of drops. The spherical coordinates (r, θ, ϕ) are chosen with its origin located at the center of the drop. We assume that the dispersion medium is Newtonian and incompressible and has constant physical

properties, and the dispersed phase comprises an incompressible Carreau fluid, which is electrolyte-free and has constant physical properties. The system is assumed to remain in a quasi-steady state.

The constitutive equation of a generalized Newtonian fluid can be expressed as

$$\boldsymbol{\tau} = -\eta(\dot{\gamma})\dot{\boldsymbol{\gamma}}, \quad (1)$$

$$\dot{\boldsymbol{\gamma}} = \nabla \mathbf{v} + (\nabla \mathbf{v})^T. \quad (2)$$

In these expressions, $\boldsymbol{\tau}$ is the shear stress tensor, $\dot{\boldsymbol{\gamma}}$ is the rate of strain tensor, $\dot{\gamma}$ is its magnitude, η is the apparent viscosity, $\mathbf{v}$ is the fluid velocity, ∇ is the gradient operator, and the superscript T denotes matrix transpose. For the present Carreau fluid [23,24] we assume that

$$\eta(\dot{\gamma}) = \eta_0 [1 + (\lambda \dot{\gamma})^2]^{(n-1)/2}. \quad (3)$$

In spherical coordinates, $\dot{\gamma}$ can be expressed as

$$\dot{\gamma} = \sqrt{\frac{1}{2}(\dot{\gamma}_{rr}^2 + \dot{\gamma}_{\theta\theta}^2 + \dot{\gamma}_{\phi\phi}^2) + \dot{\gamma}_{r\theta}^2 + \dot{\gamma}_{r\phi}^2 + \dot{\gamma}_{\theta\phi}^2}, \quad (4)$$

where η_0 is the zero-shear-rate viscosity, λ is a relaxation-time constant, and n is a power-law index. Note that if $n = 1$ or $\lambda = 0$, Eq. (3) leads to a Newtonian fluid, and if $\lambda \dot{\gamma} \gg 1$, it yields a power-law fluid.

The electrophoresis problem under consideration can be described by the electrokinetic equations, which include the equations for the electric field, the flow field, and the concentration field.

2.1. Electric field

According to Gauss's law, the electrical potential ϕ can be described by the Poisson equation,

$$\nabla^2 \phi = -\frac{\rho_e}{\varepsilon} = -\frac{1}{\varepsilon} \sum_{j=1}^2 z_j e n_j, \quad (5)$$

where ∇^2 is the Laplace operator, ε is the permittivity of the dispersion medium, $\rho_e = \sum_{j=1}^2 z_j e n_j$ is the space charge density, e is the elementary charge, and z_j and n_j are respectively the valence and the number concentration of ionic species j . The spatial variation in the ionic concentration is described by

$$\nabla^2 n_j + \frac{z_j e}{kT} (\nabla n_j \cdot \nabla \phi + n_j \nabla^2 \phi) - \frac{1}{D_j} \mathbf{v} \cdot \nabla n_j = 0, \quad (6)$$

where D_j is the diffusivity of ionic species j and k and T are respectively the Boltzmann constant and the absolute temperature.

2.2. Flow field

Suppose that the flow field can be described by the Navier–Stokes equation in the creeping flow regime and by

the continuity equation. We have

$$\mu \nabla^2 \mathbf{v} - \nabla p - \rho_e \nabla \phi = 0, \quad a < r < b, \quad (7)$$

$$-\nabla p - \nabla \cdot \boldsymbol{\tau} = 0, \quad r < a, \quad (8)$$

$$\nabla \cdot \mathbf{v} = 0, \quad (9)$$

where p is the pressure, and μ is the viscosity of the dispersion medium.

For a simpler treatment, ϕ is partitioned into the electrical potential arising from the presence of a drop in the absence of $\mathbf{E}$, or the equilibrium potential ϕ_1 , and the electrical potential outside the drop arising from $\mathbf{E}$, ϕ_2 , that is, $\phi = \phi_1 + \phi_2$. For the case of low electrical potential and weak $\mathbf{E}$, it can be shown that the governing equations for ϕ_1 and ϕ_2 are

$$\nabla^2 \phi_1 = -\frac{1}{\varepsilon} \sum_j z_j e n_{j0} \left(1 - \frac{z_j e \phi_1}{kT}\right), \quad (10)$$

$$\nabla^2 \phi_2 = 0, \quad (11)$$

where n_{j0} is the bulk concentration of ionic species j . These equations can be rewritten in terms of scaled symbols as

$$\nabla^{*2} \phi_1^* = (\kappa a)^2 \phi_1^*, \quad (12)$$

$$\nabla^{*2} \phi_2^* = 0, \quad (13)$$

where $\phi_1^* = \phi_1 / \zeta_a$, $\phi_2^* = \phi_2 / \zeta_a$, $\nabla^* = a \nabla$. ζ_a is the surface potential of the drop, and $\kappa = [\sum_j n_{j0} (e z_j)^2 / \varepsilon kT]^{1/2}$ is the reciprocal Debye length.

The mathematical treatment of flow field can be simplified by introducing the stream function ψ . In terms of this function, the r - and the θ -components of fluid velocity, v_r and v_θ , can be expressed respectively as $v_r = (-1/r^2 \sin \theta)(\partial \psi / \partial \theta)$ and $v_\theta = (1/r \sin \theta)(\partial \psi / \partial r)$. Note that the continuity equation of the flow field is automatically satisfied through the introduction of ψ . The pressure terms in Eqs. (7) and (8) can be eliminated by taking curl on both sides of them. In terms of the stream function, it can be shown that the flow field can be described by

$$D^{*4} \psi^* = -(\kappa a)^2 \left(\frac{\partial \phi_1^*}{\partial r^*} \frac{\partial \phi_2^*}{\partial \theta} \right) \sin \theta, \quad 1 < r^* < 1/H, \quad (14)$$

$$\begin{aligned} \eta^* D^{*4} \psi^* + \sin \theta \left[\left(\frac{\partial \eta^*}{\partial r^*} \dot{\gamma}_{r\theta}^* + r^* \frac{\partial^2 \eta^*}{\partial r^{*2}} \dot{\gamma}_{r\theta}^* + r^* \frac{\partial \eta^*}{\partial r^*} \frac{\partial \dot{\gamma}_{r\theta}^*}{\partial r^*} \right. \right. \\ \left. \left. + \frac{\partial^2 \eta^*}{\partial r^* \partial \theta} \dot{\gamma}_{\theta\theta}^* + \frac{\partial \eta^*}{\partial \theta} \frac{\partial \dot{\gamma}_{\theta\theta}^*}{\partial r^*} \right) - \left(\frac{\partial^2 \eta^*}{\partial r^* \partial \theta} \dot{\gamma}_{rr}^* + \frac{\partial \eta^*}{\partial r^*} \frac{\partial \dot{\gamma}_{rr}^*}{\partial \theta} \right. \right. \\ \left. \left. + \frac{1}{r^*} \frac{\partial^2 \eta^*}{\partial \theta^2} \dot{\gamma}_{r\theta}^* + \frac{1}{r^*} \frac{\partial \eta^*}{\partial \theta} \frac{\partial \dot{\gamma}_{r\theta}^*}{\partial \theta} \right) + \frac{\partial \eta^*}{\partial r^*} \left(\frac{1}{\sin \theta} \frac{\partial^3 \psi^*}{\partial r^{*3}} \right. \right. \\ \left. \left. - \frac{\cot \theta}{r^{*2} \sin \theta} \frac{\partial^2 \psi^*}{\partial r^* \partial \theta} + \frac{1}{r^{*2} \sin \theta} \frac{\partial^3 \psi^*}{\partial r^* \partial \theta^2} \right. \right. \\ \left. \left. - \frac{2}{r^{*3} \sin \theta} \frac{\partial^2 \psi^*}{\partial \theta^2} + \frac{2 \cot \theta}{r^{*3} \sin \theta} \frac{\partial \psi^*}{\partial \theta} \right) \right] \end{aligned}$$

$$\begin{aligned}
& -\frac{\partial \eta^*}{\partial \theta} \left(-\frac{1}{r^{*2} \sin \theta} \frac{\partial^3 \psi^*}{\partial r^{*2} \partial \theta} - \frac{1}{r^{*4} \sin \theta} \frac{\partial^3 \psi^*}{\partial \theta^3} \right. \\
& \left. - \frac{1}{r^{*4} \sin^3 \theta} \frac{\partial \psi^*}{\partial \theta} + \frac{\cot \theta}{r^{*4} \sin \theta} \frac{\partial^2 \psi^*}{\partial \theta^2} \right) \Bigg] \\
& = 0, \quad 0 < r^* < 1,
\end{aligned} \quad (15)$$

where $D^{*4} = D^{*2} D^{*2}$ with

$$D^{*2} = a^2 D^2 = a^2 \left(\frac{\partial}{\partial r^2} + \frac{\sin \theta}{r^2} \frac{\partial}{\partial \theta} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \right) \right). \quad (16)$$

In these expressions, $H = a/b$, $r^* = r/a$, $\psi^* = \psi/(U_E a^2)$, $U_E = \varepsilon \zeta_a^2 / \mu a$, $\dot{\gamma}^* = a \dot{\gamma} / U_E$, and $\eta^* = \eta / \eta_0$.

2.3. Boundary conditions

The following boundary conditions are assumed for the equilibrium potential ϕ_1 :

$$\phi_1 = \zeta_a, \quad r = a, \quad (17)$$

$$\frac{\partial \phi_1}{\partial r} = 0, \quad r = b. \quad (18)$$

The first condition implies that the drop surface remains at a constant potential. The second condition arises from the basic idea of the present cell model: a cell is a representative of the whole dispersion; across the cell boundary. In terms of scaled symbols, these conditions become

$$\phi_1^* = 1, \quad r^* = 1, \quad (19)$$

$$\frac{\partial \phi_1^*}{\partial r^*} = 0, \quad r^* = 1/H. \quad (20)$$

The following boundary conditions are assumed for the perturbed potential ϕ_2 :

$$\frac{\partial \phi_2}{\partial r} = 0, \quad r = a, \quad (21)$$

$$\frac{\partial \phi_2}{\partial r} = -E_z \cos \theta, \quad r = b. \quad (22)$$

The first expression is based on the fact that drops are non-conductive and are impermeable to ionic species. The second expression arises again from the nature of the present cell model; that is, since the cell boundary corresponds to the system boundary, the electric field there is that contributed by the applied electric field only. In terms of scaled symbols, these conditions become

$$\frac{\partial \phi_2^*}{\partial r^*} = 0, \quad r^* = 1, \quad (23)$$

$$\frac{\partial \phi_2^*}{\partial r^*} = -E_z^* \cos \theta, \quad r^* = 1/H, \quad (24)$$

where $E_z^* = E_z / (\zeta_a / a)$.

We assume that both the velocity and the shear stress are continuous across the drop-dispersion medium interface; that is,

$$v_\theta|_{r=a^+} = v_\theta|_{r=a^-}, \quad (25)$$

$$\tau_{r\theta}|_{r=a^+} = \tau_{r\theta}|_{r=a^-}, \quad (26)$$

where $\tau_{r\theta}$ is the $r\theta$ -component of the shear stress tensor. In terms of the stream function, it can be shown that these expressions become

$$\frac{\partial \psi}{\partial r} \Big|_{r=a^+} = \frac{\partial \psi}{\partial r} \Big|_{r=a^-}, \quad (27)$$

$$\begin{aligned}
& \eta_0 [1 + (\lambda \dot{\gamma}^*)^2]^{(n-1)/2} \\
& \times \left[\frac{1}{r} \frac{\partial^2}{\partial r^2} - \frac{2}{r^2} \frac{\partial}{\partial r} - \frac{1}{r^3} \frac{\partial^2}{\partial \theta^2} + \frac{\cos \theta}{r^3 \sin \theta} \frac{\partial}{\partial \theta} \right] \psi|_{r=a^+} \\
& = \mu \left[\frac{1}{r} \frac{\partial^2}{\partial r^2} - \frac{2}{r^2} \frac{\partial}{\partial r} - \frac{1}{r^3} \frac{\partial^2}{\partial \theta^2} + \frac{\cos \theta}{r^3 \sin \theta} \frac{\partial}{\partial \theta} \right] \psi|_{r=a^-}.
\end{aligned} \quad (28)$$

Also, since a drop moves with velocity U in the z -direction, the condition below needs to be satisfied on the drop surface:

$$\psi = -\frac{1}{2} U r^2 \sin \theta, \quad r = a. \quad (29)$$

The following conditions are assumed on the cell surface:

$$v_r = 0 \quad \text{and} \quad \nabla \times \mathbf{v} = 0, \quad r = b. \quad (30)$$

The first expression arises from the fact that there is no net flow of fluid across the cell boundary, and the second condition is one of the key properties of Kuwabara's unit cell model. In terms of the stream function, we have

$$\begin{aligned}
& \psi = \left(\frac{1}{r \sin \theta} \frac{\partial^2}{\partial r^2} - \frac{\cos \theta}{r^3 \sin^2 \theta} \frac{\partial}{\partial \theta} + \frac{1}{r^3 \sin \theta} \frac{\partial^2}{\partial \theta^2} \right) \psi = 0, \\
& r = b.
\end{aligned} \quad (31)$$

Expressing Eqs. (27), (28), (29), and (31) in terms of scaled symbols, we have

$$\frac{\partial \psi^*}{\partial r^*} \Big|_{r^*=1^+} = \frac{\partial \psi^*}{\partial r^*} \Big|_{r^*=1^-}, \quad (32)$$

$$\begin{aligned}
& \frac{\eta_0}{\mu} [1 + (\lambda^* \dot{\gamma}^*)^2]^{(n-1)/2} \left[\frac{1}{r^*} \frac{\partial^2}{\partial r^{*2}} - \frac{2}{r^{*2}} \frac{\partial}{\partial r^*} - \frac{1}{r^{*3}} \frac{\partial^2}{\partial \theta^2} \right. \\
& \left. + \frac{\cos \theta}{r^{*3} \sin \theta} \frac{\partial}{\partial \theta} \right] \psi^*|_{r^*=1^+} \\
& = \left[\frac{1}{r^*} \frac{\partial^2}{\partial r^{*2}} - \frac{2}{r^{*2}} \frac{\partial}{\partial r^*} - \frac{1}{r^{*3}} \frac{\partial^2}{\partial \theta^2} + \frac{\cos \theta}{r^{*3} \sin \theta} \frac{\partial}{\partial \theta} \right] \\
& \times \psi^*|_{r^*=1^-},
\end{aligned} \quad (33)$$

$$\psi^* = -\frac{1}{2} U^* r^{*2} \sin \theta, \quad r^* = 1, \quad (34)$$

$$\begin{aligned}
& \psi^* = \left(\frac{1}{r^* \sin \theta} \frac{\partial^2}{\partial r^{*2}} - \frac{\cos \theta}{r^{*3} \sin^2 \theta} \frac{\partial}{\partial \theta} + \frac{1}{r^{*3} \sin \theta} \frac{\partial^2}{\partial \theta^2} \right) \psi^* \\
& = 0, \quad r^* = 1/H,
\end{aligned} \quad (35)$$

where $\lambda^* = U_E \lambda / a$ and $U^* = U / U_E$. Here, the ratio η_0 / μ is assigned the value of unity; that is, the zero-shear-rate viscosity of the present Carreau fluid is the same as the viscosity of the dispersion medium. The symmetric nature of the present problem also requires that

$$\frac{\partial \phi_1}{\partial \theta} = \frac{\partial \phi_2}{\partial \theta} = \psi = \frac{\partial \psi}{\partial \theta} = 0, \quad \theta = 0 \text{ and } \theta = \pi/2 \quad (36)$$

or in terms of scaled symbols,

$$\frac{\partial \phi_1^*}{\partial \theta} = \frac{\partial \phi_2^*}{\partial \theta} = \psi^* = \frac{\partial \psi^*}{\partial \theta} = 0, \quad \theta = 0 \text{ and } \theta = \pi/2. \quad (37)$$

2.4. Electrophoretic mobility

The electrophoretic mobility of a drop can be evaluated based on the fact that the net force acting on it vanishes at steady state. For the present problem, only the z -component of the net force, which includes the electrical contribution, F_{Ez} , and the hydrodynamic contribution, F_{Dz} , needs to be considered. The z -component of the electrical force acting on a drop can be evaluated by [25]

$$\begin{aligned} F_{Ez} &= \int \sigma (-\nabla \phi)_s \cdot \mathbf{i}_z dA \\ &= \int \varepsilon (\nabla \phi \cdot \mathbf{n})_s (\nabla \phi \cdot \mathbf{i}_z)_s dA, \end{aligned} \quad (38)$$

where σ is the surface charge density, $\mathbf{n}$ is the unit normal vector on the drop surface, and the subscript s denotes the drop surface. In spherical coordinates, $dA = 2\pi r^2 \sin \theta d\theta$, and it can be shown that

$$\begin{aligned} F_{Ez} &= 2\pi \varepsilon \zeta_a^2 \int_0^\pi \left(\frac{\partial \phi^*}{\partial r^*} \right)_{r^*=1} \\ &\quad \times \left(\frac{\partial(\phi^*)}{\partial r^*} \cos \theta - \frac{1}{r^*} \frac{\partial(\phi^*)}{\partial \theta} \sin \theta \right)_{r^*=1} r^{*2} \sin \theta d\theta. \end{aligned} \quad (39)$$

Applying the relations $\phi^* = \phi_1^* + \phi_2^*$, $(\partial \phi_1^* / \partial \theta)_{r^*=1} = 0$, and $(\partial \phi_2^* / \partial r^*)_{r^*=1} = 0$, this expression becomes

$$\begin{aligned} F_{Ez} &= 2\pi \varepsilon \zeta_a^2 \int_0^\pi \left(\frac{\partial \phi^*}{\partial r^*} \right)_{r^*=1} \\ &\quad \times \left(-\frac{1}{r^*} \frac{\partial(\phi_2^*)}{\partial \theta} \sin \theta \right)_{r^*=1} r^{*2} \sin \theta d\theta. \end{aligned} \quad (40)$$

The z -component of the hydrodynamic force acting on a drop includes the drag on a charge-free drop, F_z , and that arising from the presence of charge on its surface. The former can be evaluated based on the results of Happel and Brenner [25]. It can be shown that

$$\begin{aligned} F_{Dz} &= \mu \pi \int_0^\pi \left(r^4 \sin^3 \theta \frac{\partial}{\partial r} \frac{E^2 \psi}{r^2 \sin^2 \theta} \right)_{r=a} d\theta \\ &\quad - \pi \int_0^\pi \left(r^2 \sin^2 \theta \frac{\partial \phi}{\partial \theta} \rho \right)_{r=a} d\theta. \end{aligned} \quad (41)$$

The first term on the right-hand side of this expression is F_z . In terms of scaled symbols this expression becomes

$$\begin{aligned} F_{Dz} &= \pi \varepsilon \zeta_a^2 \int_0^\pi \left(r^{*4} \sin^3 \theta \frac{\partial}{\partial r^*} \frac{E^{*2} \psi^*}{r^{*2} \sin^2 \theta} \right)_{r^*=1} d\theta \\ &\quad + \pi \varepsilon \zeta_a^2 (\kappa a)^2 \int_0^\pi \left(r^{*2} \sin^2 \theta \frac{\partial \phi_2^*}{\partial \theta} \phi_1^* \right)_{r^*=1} d\theta. \end{aligned} \quad (42)$$

In steady state, $F_{Ez} + F_{Dz} = 0$.

The governing equations and the associated boundary conditions are solved numerically by a pseudo-spectral method [11], which has many desirable properties such as a fast rate of convergence and convergence properties independent of boundary conditions. The present problem is of a two-dimensional nature, and for a simpler numerical treatment, the spherical domain is first mapped to a rectangular domain, and the pseudo-spectral method is then employed. A Newton–Raphson iteration scheme is adopted to solve nonlinear algebraic equations.

3. Results and discussion

The influence of the key parameters of the system under consideration on its electrophoretic behavior is examined through numerical simulation. These include the shear-thinning nature of the drop fluid, the thickness of the double layer, and the concentration of a dispersion. The influence of the shear-thinning nature of the drop fluid on the mobility of a drop is illustrated in Fig. 3, where the variation of the scaled mobility μ_m^* as a function of κa at various n is presented for two levels of λ^* . Note that if $n = 1.0$, the drop is Newtonian. Fig. 3 suggests that μ_m^* increases with κa , in general. This is because a large κa means that the double layer surrounding a drop is thin. In this case the absolute value of the potential gradient near the drop surface is large, which yields a large electrical force acting on the drop, and the mobility becomes large accordingly. If κa is small, the double layer surrounding a drop is thick. In this case, the electrical interaction between neighboring double layers becomes important, which has the effect of prohibiting the movement of a drop. It is expected that $\mu_m^* \rightarrow 0$ as $\kappa a \rightarrow 0$, and the mobility is insensitive to the nature of the drop, as justified in Fig. 3. If κa is sufficiently large, the nature of the drop becomes important; that is, the effect of shear thinning is significant. In this case, the greater the effect of shear thinning is, the less the hydrodynamic drag acting on a drop is and, therefore, the larger its mobility is. This is why Fig. 3 shows that μ_m^* is large if n is small and/or λ^* is large.

The influence of the concentration of drops on their mobility is presented in Fig. 4, where the variation of the scaled mobility μ_m^* as a function of κa at various H is plotted. This figure reveals that for both very thick (small κa) and very thin double layers (large κa), the mobility is insensitive to

Fig. 3. Variation of scaled mobility μ_m^* as a function of κa at various n for the case $H = 0.5$, $E_z^* = 1.0$, and $\alpha = 1$: (a) $\lambda^* = 0.5$, (b) $\lambda^* = 1.5$.

the variation in H , and for a medium-thickness double layer, the larger H is, the smaller the mobility is. As in Fig. 3, if the double layer surrounding a drop is thick, the electrical interaction between neighboring double layers leads to a small mobility. On the other hand, if the double layer surrounding a drop is thin, the absolute value of the potential gradient near its surface becomes large, which is advantageous to its movement. In this case, although a large H will prohibit the movement of a drop hydrodynamically, its electrophoresis is mainly controlled by the potential gradient near its surface and therefore is H -insensitive. For the case of a medium-thickness double layer, the larger H is, the more significant the hydrodynamic retardation of neighboring drops is and, therefore, the smaller the mobility is.

Fig. 5 shows the typical contours of the scaled stream function ψ^* . Note that in the present problem, the drop in a representative cell moves in the z -direction relative to the dispersion medium in the cell. For convenience, we let the origin of the coordinates be located at the center of the drop. This is equivalent to saying that the drop is fixed and the dispersion medium moves in the $-z$ -direction. As can be seen in Fig. 5, the movement of the drop in the z -direction yields a counterclockwise flow on its right-hand side and a clock-

Fig. 4. Variation of scaled mobility μ_m^* as a function of κa at various H for the case when $n = 0.9$, $\lambda^* = 0.5$, $E_z^* = 1.0$, and $\alpha = 1$.

Fig. 5. Contours of the scaled stream function for the case when $n = 0.9$, $\lambda^* = 1.0$, $\kappa a = 5.01187$, $H = 0.5$, $E_z^* = 1.0$, and $\alpha = 1$.

wise flow on its left-hand side (not shown). In contrast, the flow of fluid inside the drop is clockwise on its right-hand side and counterclockwise on its left-hand side (not shown).

According to Saito [26], for the case of creeping flow, that is, as the Reynolds number, Re , approaches zero, the shape of a drop remains spherical. This is also confirmed by Taylor and Acrivos [27], who showed that the deformation of a drop is proportional to Re^2 , or to the Weber number, $We = \rho U^2 a / \sigma_1$, σ_1 being the surface tension of the drop liquid. In our case, because a typical value of Re is on the order of 10^{-10} – 10^{-8} and that of We is on the order of 10^{-17} (see Appendix A), the deformation of a drop can be neglected. In a study of the behavior of a relatively large, stationary drop in an applied electric field, Eow et al. [28] observed that breakup occurs to a drop of 1.2 mm diameter when the electric Weber number $We_e = 2\epsilon E^2 a / \sigma_1$ reaches 0.49. The mechanism behind the breakup phenomenon is the onset of instability caused by the disruptive electric-induced stress over the stabilizing interfacial tension stress. As illustrated

in Appendix A, typical We_e in our case is on the order of 10^{-8} – 10^{-5} , implying that the deformation of a drop is negligible.

4. Conclusion

The electrophoresis of a concentrated aqueous dispersion of monodisperse drops containing a Carreau fluid is analyzed under conditions of low surface potential and weak electric field. This is the first attempt at the description of the electrophoretic behavior of a dispersion containing non-Newtonian drops. A system of this nature has wide applications in practice, especially for emulsions and microemulsions. The results of numerical simulation reveal that the mobility of a drop increases with the decrease in the thickness of the double layer surrounding it, which is similar to the behavior of a rigid dispersion. In general, because the shear-thinning nature of a Carreau fluid has the effect of reducing the hydrodynamic drag acting on a drop, its mobility increases accordingly, and this effect is pronounced as the thickness of the double layer decreases. However, if the double layer is sufficiently thick, this effect is negligible. In general, the higher the concentration of drops is, the smaller the mobility is; however, if the double layer is either sufficiently thin or sufficiently thick, this effect becomes unimportant.

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Appendix A

The Reynolds number Re , the Weber number We , and the electrical Weber number We_e are defined respectively by $Re = \rho U a / \mu$, $We = \rho U^2 a / \sigma_1$, and $We_e = 2 \varepsilon E^2 a / \sigma_1$, σ_1 being the surface tension of the drop liquid. In our case, we have $\mu_m^* = U^* / E^*$, $E^* = E / (\zeta_a / a)$, and $E = E^* (\zeta_a / a)$. Also, $U^* = U / U_E = U / (\varepsilon \zeta_a^2 / \mu a)$, $U = U^* (\varepsilon \zeta_a^2 / \mu a)$, $U^* = \mu_m^* E^* = U / (\varepsilon \zeta_a^2 / \mu a)$, and $U = \mu_m^* E^* (\varepsilon \zeta_a^2 / \mu a)$. For a sunflower oil drop at 1 atm and 20 °C [28], $\varepsilon = 4.34 \times$

10^{-11} F/m, $\mu = 4.72 \times 10^{-2}$ Pa s, $\rho = 992$ kg/m³, and σ_1 (oil–water) = 1.6×10^{-2} N/m. If we choose the typical values $\mu_m^* = 1$, $E^* = 1$, $a = 10^{-7}$ m, $\zeta_a = 25.6$ mV, $E = E^* \zeta_a / a = 256$ kV/m, and $U = 1.0 \times 10^{-7}$ m/s, then $Re = 2.10 \times 10^{-10}$, $We = 6.20 \times 10^{-17}$, and $We_e = 3.55 \times 10^{-5}$. Similarly, for an *n*-heptane drop at 1 atm and 20 °C [28], $\varepsilon = 1.77 \times 10^{-11}$ F/m, $\mu = 4.21 \times 10^{-4}$ Pa s, $\rho = 682$ kg/m³, σ_1 and (HPLC–water) = 2.6×10^{-2} N/m. Therefore, using the same set of μ_m^* , E^* , a , ζ_a , E , and U as for a sunflower oil drop, we obtain $Re = 1.62 \times 10^{-8}$, $We = 2.62 \times 10^{-17}$, and $We_e = 8.92 \times 10^{-8}$.

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