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Effect of a Charged Boundary on Electrophoresis in a Carreau Fluid: A Sphere at an Arbitrary Position in a Spherical Cavity

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The influence of a charged boundary on the electrophoretic behavior of an entity in a non-Newtonian fluid is studied by considering a sphere at an arbitrary position in a spherical cavity filled with a Carreau fluid under the conditions of low surface potential and weak applied electric field. The dependence of the mobility of a sphere on its position in a cavity, the size of a cavity, the thickness of a double layer, and the nature of a fluid is investigated. In addition to the fact that the effect of shear-thinning is advantageous to the movement of a sphere, several other interesting results are also observed. For instance, if an uncharged sphere is in a positively charged cavity, where the electroosmotic flow and the induced charge on the sphere surface play a role, the effect of shear-thinning is important only if the thickness of the double layer is either sufficiently thin or sufficiently thick. However, this might not be the case if a positively charged sphere is in an uncharged cavity.

1. Introduction

Since the pioneer work of Smoluchowski¹ in the early stage of the last century, electrophoresis has been adopted widely in many fields, both as an analytical tool to characterize the surface properties of an entity and as an operation to differentiate or separate entities of various natures. One of the key factors that often need to be considered in conducting electrophoresis is the presence of a boundary. In capillary electrophoresis and electrophoresis of particles through a porous medium, this effect should not be neglected. In addition to the fact that the degree of difficulty in solving the governing equations with associated boundary conditions increases appreciably when the boundary effect is important, care must be taken in the elaboration of the experimental data gathered because they are usually of complicated nature. The boundary effect on electrophoresis has been studied in many papers considering various types of geometry.^{2–10} Apparently, because both the fluid and the electric fields near a particle are influenced by a boundary, which is sufficiently close, so is the electrophoretic behavior of the particle. If a boundary is charged, then three additional effects need to be considered, namely the presence of an electroosmotic flow field,^{2–4,10–17} an osmotic pressure field,^{2–4,10–18} and the charge induced on the particle surface. These effects can influence significantly, both quantitatively and qualitatively, the electro-

phoretic behavior of a particle. For instance, the presence of a charged boundary may alter the direction of the electrophoresis of a particle,^{2–4,10,18} and the electrophoretic mobility of a particle can exhibit a local maximum or minimum as the thickness of the double layer varies.^{12–18} Apparently, these results are of practical importance in the cases where electrophoresis is adopted as a separation tool. Typical examples in which a charged boundary can play a role include capillary electrophoresis in a fused silica pore, which is negatively charged due to the dissociation of the silanol group,^{19,20} and microchip electrophoresis where the wall surface is modified by a polymer coating, which can yield either a positively or negatively charged surface.²¹

Although previous analyses on electrophoresis focused mainly on the case in which the liquid phase is a Newtonian fluid, electrophoresis involving a non-Newtonian fluid is not uncommon in practice. The addition of surfactant or polymer to improve the stability of a colloidal dispersion,²² for example, can lead to a shear-thinning non-Newtonian fluid. These substances are also utilized as additives to the electrolyte solutions employed in protein or DNA capillary zone electrophoresis to minimize protein–capillary or DNA–capillary wall interaction, so that the selectivity and the resolution are improved and the electroosmotic flow is controlled.^{20,23} The elevation of the concentration of dispersed particles can also yield a non-Newtonian fluid. A typical example for this is the slurry used in chemical mechanical polishing.²⁴ Lee et al.²⁵ initiated the analysis of electrophoresis in a non-Newtonian fluid by considering a rigid sphere at the center of a spherical cavity filled with a Carreau fluid under the conditions of low surface potential and weak applied electric field. Their analysis was extended by Hsu et al.²⁶

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Figure 1. Schematic representation of the problem considered where a sphere of radius a is placed at an arbitrary position in a spherical cavity of radius b filled with a Carreau fluid. The cylindrical coordinates (r, θ, z) are adopted with the origin located at the center of the cavity. A uniform electric field $\mathbf{E}$ parallel to the z -direction is applied. The center of the sphere is at $z = m$.

to the case in which a rigid sphere is at an arbitrary position in a spherical cavity. Hsu et al.²⁷ studied the electrophoresis of a dispersion of rigid spheres in a Carreau fluid under the condition of low surface potential. Their analysis was extended by Lee et al.²⁸ to the case of an arbitrary surface potential. The electrophoresis of a rigid sphere in a Carreau fluid normal to a planar surface was considered by Lee et al.,²⁹ and that along the axis of a cylindrical pore was studied by Hsu et al.³⁰ In general, the shear-thinning nature of a fluid is advantageous to the electrophoresis of a particle, and the thinner the double layer surrounding a particle, the more significant the effect of shear-thinning.^{25–30}

In this study, the presence of a charged boundary on the electrophoretic behavior of a particle in a non-Newtonian fluid is analyzed by considering the electrophoresis of a sphere at an arbitrary position in a spherical cavity filled with a Carreau fluid under the conditions of low surface potential and weak applied electric field. Protein²⁰ or DNA^{23,31,32} separation, for example, involves this type of problem. The influences of the size of a cavity, the position of a sphere in a cavity, the thickness of a double layer, and the properties of a fluid on the electrophoretic behavior of a sphere are discussed.

2. Theory

As shown in Figure 1, let us consider the electrophoresis of a rigid sphere of radius a at an arbitrary position in a spherical cavity of radius b filled with a Carreau fluid. The cylindrical coordinates (r, θ, z) are chosen with the origin located at the center of the cavity, and the center of the sphere is at $z = m$. A uniform electric field $\mathbf{E}$ of strength E in the z -direction is applied. Since the present problem is θ -symmetric, only the (r, z) domain has to be considered. We assume that the present system is at a pseudosteady state;^{2,4,11} that is, the terms that

involve the time derivative in the governing equations can be neglected. Under the conditions of weak applied electric field and low surface potential, it can be shown that the electric potential of the present system, Ψ , can be decomposed into an equilibrium potential in the absence of $\mathbf{E}$, Ψ_1 , and a distributed potential outside the sphere arising from $\mathbf{E}$, Ψ_2 , and these potentials satisfy³³

$$\nabla^2 \Psi_1 = \kappa^2 \Psi_1 \quad (1)$$

and

$$\nabla^2 \Psi_2 = 0 \quad (2)$$

Here, ∇^2 is the Laplace operator, $\kappa = [\sum_j n_j^0 (ez_j)^2 / \epsilon k_B T]^{1/2}$ is the reciprocal Debye length, n_j^0 and z_j are the bulk number concentration and the valence of ionic species j , respectively, and ϵ , e , k_B , and T are the permittivity of the liquid phase, the elementary charge, the Boltzmann constant, and the absolute temperature, respectively. The assumption of weak applied electric field is usually satisfied for conditions of practical significance,³⁴ and that of low surface potential is appropriate if the surface potential is lower than ~ 25 mV.

Suppose the sphere and the cavity are held at constant surface potentials ζ_p and ζ_w , respectively. Also, the sphere surface is nonconductive and the local electric field on the cavity surface is that caused by the applied electric field.² The boundary conditions associated with eqs 1 and 2 are then

$$\Psi_1 = \zeta_p \text{ on the sphere surface} \quad (3)$$

$$\Psi_1 = \zeta_w \text{ on the cavity surface} \quad (4)$$

$$\mathbf{n} \cdot \nabla \Psi_2 = 0 \text{ on the sphere surface} \quad (5)$$

$$\mathbf{n} \cdot \nabla \Psi_2 = -E \cos \theta \text{ on the cavity surface} \quad (6)$$

where $\mathbf{n}$ is the unit normal vector directed into the liquid phase.

For an incompressible fluid, the flow field at steady state can be described by³⁵

$$\nabla \cdot \mathbf{u} = 0 \quad (7)$$

and

$$-\nabla \cdot \boldsymbol{\tau} - \nabla p = -\rho_e \mathbf{E} \quad (8)$$

Here, $\mathbf{E} = -\nabla \Psi_2$, $\mathbf{u}$ and p are the velocity and the pressure of the liquid phase, respectively, $-\rho_e \mathbf{E} = \rho_e \nabla \Psi_2$ is the electric body force acting on the fluid,^{9–12,17,34,38}

$$\rho_e = \sum_j z_j e n_j^0 \exp[-z_j e \Psi / k_B T]$$

is the space charge density, and the stress tensor $\boldsymbol{\tau}$ can be expressed as

$$\boldsymbol{\tau} = -\eta(\dot{\gamma}) \dot{\boldsymbol{\gamma}} \quad (9)$$

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Figure 2. Variation of the scaled electrophoretic mobility μ^* as a function of κa at various position parameter P values with $\lambda = 0.5$ (a) and as a function of P at various λ values with $\kappa a = 1$ (b) for the case in which a sphere of constant scaled surface potential ζ_p^* ($= \zeta_p/(k_B T/e)$) is placed in an uncharged spherical cavity. Solid curves represent results for a Newtonian fluid and dashed curves represent results for a Carreau fluid with (a) $n = 0.8$ and $\alpha U/a = 0.5$ and (b) $n = 0.8$ and $\alpha U/a = 0.8$. (●) Analytical result of Zydney;² (○) numerical result of Lee et al.;²⁵ (■ and □) numerical results of Hsu et al.²⁶ for a Newtonian fluid and a Carreau fluid with $n = 0.8$ and $\alpha U/a = 0.8$, respectively.

Figure 3. Variation of the scaled electrophoretic mobility μ^* as a function of the position parameter P at various λ values (a) and as a function of λ at various P values (b) for the case of an uncharged sphere in a positively charged spherical cavity at $\zeta_p^* = 0$, ζ_w^* ($= \zeta_w/(k_B T/e)$) = 1, and $\kappa a = 1$. Solid curves represent results for a Newtonian fluid and dashed curves represent results for a Carreau fluid with $n = 0.8$ and $\alpha U/a = 0.8$.

where $\dot{\gamma} = \nabla \mathbf{u} + (\nabla \mathbf{u})^T$ is the rate of strain tensor, $\dot{\gamma}$ is its magnitude, $\eta(\dot{\gamma})$ is the viscosity, and the superscript **T** denotes matrix transpose.³⁵ Suppose the liquid phase is a Carreau fluid, the viscosity of which can be expressed as^{35,36}

$$\eta(\dot{\gamma}) = \eta_\infty + (\eta_0 - \eta_\infty)[1 + (\alpha\dot{\gamma})^\beta]^{(n-1)/\beta} \quad (10)$$

Here, η_0 and η_∞ are the viscosities corresponding to the zero shear rate and the infinite shear rate, respectively, α is the relaxation time constant, n is the power-law index, and β is a dimensionless parameter that describes the transition region between the zero-shear-rate region and the power-law region. According to eq 10, the variation of $\eta(\dot{\gamma})$ can be divided into three regions:^{35,36} (i) For small $\dot{\gamma}$, η is insensitive to the variation of $\dot{\gamma}$, the so-called zero-shear-rate viscosity region. (ii) If $\dot{\gamma}$ exceeds a critical value, η decreases monotonically with $\dot{\gamma}$, the so-called power-law fluid region. (iii) If $\dot{\gamma}$ is large, η becomes insensitive to the variation of $\dot{\gamma}$, the so-called infinite-shear-rate viscosity

region. Under conditions of practical significance, $\beta = 2$ and $\eta_\infty = 0$,^{35,36} and eq 10 reduces to

$$\eta(\dot{\gamma}) = \eta_0[1 + (\alpha\dot{\gamma})^2]^{(n-1)/2} \quad (11)$$

Note that if $n = 1$ and/or $\alpha = 0$, the present fluid becomes a Newtonian fluid, and if α is sufficiently large, it becomes a power-law fluid. If both the surface of a sphere and that of the cavity are no-slip, then the boundary conditions associated with eqs 7 and 8 are

$$\mathbf{u} = U\mathbf{e}_z \text{ on the sphere surface} \quad (12)$$

$$\mathbf{u} = 0 \text{ on the cavity surface} \quad (13)$$

where U is the magnitude of sphere velocity in the z -direction and $\mathbf{e}_z$ is the unit vector in the z -direction.

In the present case, only the z -components of the forces acting on a sphere need to be considered. These include the electric

Figure 4. Typical flow fields for a Carreau fluid with $n = 0.8$ and $\alpha U/a = 0.8$ for the case of Figure 3: (a) $P = 60\%$ and $\lambda = 0.2$; (b) $P = 95\%$ and $\lambda = 0.2$; (c) $P = 60\%$ and $\lambda = 0.6$.

force and the hydrodynamic force. Applying our recent result,^{9,34} the z -component of the former, F_E , can be calculated by^{9–12,15,17,18,34,38}

$$F_E = \iint_S \sigma_p E_z \, dS \quad (14)$$

where S denotes the sphere surface, $\sigma_p = -\epsilon \mathbf{n} \cdot \nabla \Psi_1$ is the charge density on S , and $E_z = -\partial \Psi_2 / \partial z$ is the strength of the local applied electric field in the z -direction. The hydrodynamic force acting on a sphere in the z -direction, F_D , can be evaluated by^{34,37}

$$F_D = \iint_S \eta \frac{\partial(\mathbf{u} \cdot \mathbf{t})}{\partial n} t_z \, dS + \iint_S -pn_z \, dS \quad (15)$$

where $\mathbf{t}$ is the unit tangential vector on S , n is the magnitude of $\mathbf{n}$, and t_z and n_z are the z -component of $\mathbf{t}$ and that of $\mathbf{n}$, respectively. At steady state, the total force acting on a sphere in the z -direction vanishes, that is,

$$F_E + F_D = 0 \quad (16)$$

This expression can be used to calculate the electrophoretic mobility of a sphere.^{6,38}

3. Results and Discussion

FlexPDE,³⁹ a differential equation solver based on a finite element scheme, is adopted for the resolution of the governing equations and the associated boundary conditions. The applicability of this software is justified by considering the electrophoresis of a positively charged sphere of fixed radius in an uncharged spherical cavity analyzed previously in the literature. Figure 2 summarizes the available results^{2,25,26} for the scaled electrophoretic mobility of a sphere μ^* and the corresponding results based on the software used. Here, μ^* is defined as $\mu^* = U\eta/\zeta_{\text{ref}}\epsilon E$, with $\zeta_{\text{ref}} = k_B T/e$ being a reference potential, κa is the scaled thickness of a double layer, the position parameter P ($= 100m/(b - a)\%$) represents the relative position of a sphere in a cavity, and λ ($= a/b$) is the relative size of a sphere. Apparently, the larger the P and/or λ , the more significant the boundary effect is. Note that $P = 0\%$ and $P = 100\%$ represent, respectively, the case when a sphere is at the center of a cavity and when it touches the north pole of a cavity. According to Figure 2a, the performance of the software used in this study is satisfactory. This figure also indicates that, for both Newtonian and Carreau fluids, μ^* increases monotonically with the increase in κa , but μ^* is more sensitive to the variation of κa for a Carreau fluid. As shown in Figure 2a, the difference between the mobility in a Carreau fluid and that in the corresponding Newtonian fluid increases with the increase in κa . These are consistent with the results in the literature.^{25–30} Figure 2b reveals that, for both Newtonian and Carreau fluids, when $P = 0\%$ the present results are consistent with those in the literature. However, as P increases, they are different both qualitatively and quantitatively. This is because the formula used to evaluate the z -component of the electric force acting on a sphere, F_E , in the literature²⁶ is different from that used in this study. We have shown that^{9,34} if the geometry of a system is not totally symmetric, such as $P > 0\%$ in the present problem, an extraneous electric body force $\rho_e \nabla \Psi_1$ and an extraneous electric force arising from the equilibrium electric potential

$$\iint_S \epsilon (\partial \Psi_1 / \partial n) (\partial \Psi_1 / \partial z) \, dS$$

will be considered, thereby leading to different results. Figure 2 shows that the following conditions lead to a small mobility: the double layer is thick, a sphere is close to a cavity, and the boundary effect is significant. The rationale behind these observations will be elaborated later.

3.1. Uncharged Sphere in a Positively Charged Cavity. If an uncharged sphere is placed in a positively charged cavity, because an electroosmotic recirculation flow is generated due to the presence of the latter,^{2,10} the former experiences a

Figure 5. Contours of the scaled viscosity η^* for the case of Figure 4.

positive hydrodynamic force.¹⁰ Also, a negative charge is induced on the sphere surface as it approaches the cavity surface. Therefore, the electrophoretic behavior of a sphere is more complicated than that for the case in which a positively charged sphere is in an uncharged cavity. Figure 3 shows the variations of the scaled mobility μ^* as a function of the position parameter P and the relative size of a sphere λ ($= a/b$). For comparison, the results for the corresponding Newtonian fluid are also presented. It is interesting to note that for both Newtonian and Carreau fluids, the behavior of μ^* depends highly upon the levels of λ and/or P . For example, in Figure 3a, if λ is large, $|\mu^*|$ declines monotonically with the increase in P . If λ takes a medium value, $|\mu^*|$ has a local maximum as P varies, and if λ is small, μ^* changes its sign from positive to negative as P increases and $|\mu^*|$ has a local maximum. Figure 3b reveals that, regardless of the level of P , $|\mu^*|$ has a local maximum as λ varies. If P is large, μ^* is negative, but if P is not too large, μ^* changes its sign from positive to negative as λ increases. Therefore, we conclude that if the boundary effect is important (λ and/or P are large), μ^* is always negative. On the other hand, if it is unimportant, μ^* changes its sign from positive to negative as λ and/or P increase. Note that $\mu^* \rightarrow 0$ as $\lambda \rightarrow 1$ and/or $P \rightarrow 100\%$, as is required by the non-slip boundary condition assumed on the cavity surface. The influences of λ and P on the behavior of μ^* are the consequence of the net result of two competing factors. Electrically, because the amount of negative charge induced on the sphere surface increases with the increase in λ and/or P , the corresponding electric force acting on the sphere increases accordingly.¹⁰ Hydrodynamically, if both λ and P are not too large, the recirculation electroosmotic

flow arising from the presence of the charged cavity drives the sphere. This driving force becomes unimportant, however, if λ and/or P are too large because the viscous retardation due to the presence of the cavity dominates.¹⁰ Figure 3 shows that $|\mu^*|$ for a Carreau fluid is larger than that for the corresponding Newtonian fluid, which is expected, and can be explained by the shear-thinning effect of a Carreau fluid. This is consistent with the electroosmotic mobility of polymer solutions in a charged fused silica capillary.¹⁹ To measure the extent of the effect of shear-thinning, we define^{29,30}

$$PD = \frac{|\mu^*(\text{Carreau})| - |\mu^*(\text{Newtonian})|}{|\mu^*(\text{Newtonian})|} \times 100\% \quad (17)$$

For the case of Figure 3, if $\lambda = 0.4$, the PD values are 1.12, 1.21, 3.43, and 10.08% for $P = 0, 40, 80$, and 95%, respectively, and if $P = 60\%$, the PD values are 0.31, 1.24, 6.14, and 17.09% for $\lambda = 0.1, 0.2, 0.6$, and 0.8, respectively. That is, the larger the value of P and/or λ , the more significant the shear-thinning effect, which was not observed by Hsu et al.,²⁶ when the cavity is uncharged. This can be explained by the behavior of the flow field and the spatial variation in the scaled viscosity $\eta^* = \eta/\eta_0$ presented in Figures 4 and 5, respectively. These figures reveal that the flow field and the viscosity distribution depend highly on the levels of P and λ . For example, in Figure 4a where $P = 60\%$ and $\lambda = 0.2$, a clockwise (counterclockwise) vortex is generated on the right (left)-hand side of a sphere. However, as shown in Figure 4b, if P is raised to 95%, in addition to a clockwise vortex, a counterclockwise (clockwise) vortex is also generated on the right (left)-hand side of a sphere near the north pole of

Figure 6. Variation of the scaled electrophoretic mobility μ^* as a function of the position parameter P at various κa values (a) and as a function of κa at various P values (b). Solid curves represent results for a Newtonian fluid and dashed curves represent results for a Carreau fluid with $n = 0.8$ and $\alpha U/a = 0.8$. Key: $\zeta_p^* = 0$, $\zeta_w^* = 1$, and $\lambda = 0.4$.

the cavity. In Figure 4c, λ is raised to 0.6, and a counterclockwise (clockwise) vortex is observed on the right (left)-hand side of a sphere. Again, these phenomena are the consequence of the combined effect of the recirculation electroosmotic flow generated by the charged cavity and the negative charge induced on the sphere surface. Note that the maximal fluid velocity does not occur on the sphere surface. This is dissimilar to the case in which a positively charged sphere is in an uncharged boundary.^{25–30} The behavior of the contours of the scaled viscosity η^* shown in Figure 5 can be explained by those of the flow field illustrated in Figure 4. Figure 5a indicates that if λ is small and P is not too large, the spatial variation of η^* occurs mainly in the region right below a sphere, and the minimal η^* occurs on the lower right of the sphere surface. On the other hand, if λ and/or P are sufficiently large, the spatial variation in η^* occurs mainly in the region right above a sphere, and the minimal η^* occurs on the upper right of the sphere surface, as can be seen in Figure 5b and c. Figure 5 also suggests that, for a fixed κa , the larger the λ and/or P , the smaller the η^* , that is, the more significant the shear-thinning effect, as observed in Figure 3.

The influences of the position parameter P and the thickness of the double layer κa on the scaled mobility μ^* are shown in Figure 6. The results for the corresponding Newtonian fluid are also presented for comparison. As can be seen for both Newtonian and Carreau fluids, the behavior of μ^* depends highly upon the levels of κa and P . For example, in Figure 6a, if κa is sufficiently small ($= 0.1$), μ^* is negative and $|\mu^*|$ decreases monotonically with the increase in P . If κa takes a medium value ($= 1$), then $|\mu^*|$ has a local maximum as P varies, and if κa is large ($= 2$), μ^* changes its sign from positive to negative as P increases and $|\mu^*|$ has a local maximum. If κa is sufficiently large ($= 2$), μ^* is positive and declines monotonically with the increase in P . Figure 6b reveals that, for a fixed P , μ^* changes its sign from negative to positive as κa increases, and the value of κa at which μ^* changes its sign increases with the increase in P . The observations in Figure 6 can be explained as follows. The amount of negative charge induced on the sphere surface increases with the decrease in κa and/or the increase in P , and the corresponding electric force (negative) acting on the sphere increases accordingly.¹⁰ As κa becomes larger, due to a less serious overlap between the sphere and the double layer near a cavity, the recirculation electroosmotic flow becomes more significant and dominates the movement of the sphere. This is consistent with the result shown in Figure 4a where λ is small and P is not too

large. If P is large, the effect of the viscous retardation force due to the presence of a cavity becomes significant, leading to a decrease in $|\mu^*|$. Note that for $P = 60\%$, the values of PD are 3.59, 1.50, 0.36, and 10.99% for $\kappa a = 0.1, 1, 2$, and 5, respectively, implying that the effect of the shear-thinning becomes significant when the thickness of the double layer is either sufficiently thin or sufficiently thick. This phenomenon has not been reported previously, and it is inconsistent with the relevant theoretical results in the literature,^{25–30} where it was concluded that, for an uncharged boundary, the larger the κa , the more significant the shear-thinning effect. The effect of shear-thinning can also be justified by examining the contours of η^* shown in Figure 7. This figure indicates that the viscosity of the fluid near a sphere is small when κa is either sufficiently large or sufficiently small. This is because the smaller the κa , the larger the amount of negative charge induced on the sphere surface and the greater the electric force acting on the sphere, yielding a larger $|\mu^*|$ and a greater variation in the velocity gradient. On the other hand, the larger the κa , the faster the recirculation electroosmotic flow, which also leads to a larger μ^* and a greater shear rate. Note that if κa is not too large, the minimal viscosity occurs on the sphere surface, as shown in Figure 7a–c, which is consistent with the results reported in the literature;^{27,29,30} however, if κa is sufficiently large, the minimal viscosity occurs on the cavity surface, as illustrated in Figure 7d. This is because the thinner the double layer of the cavity, the faster the recirculation electroosmotic flow generated in that layer, thereby leading to a greater shear rate.

The influence of the nature of a Carreau fluid on the scaled electrophoretic mobility of a sphere μ^* is illustrated in Figures 8 and 9. In general, the qualitative behaviors of μ^* as P and κa vary are similar to those for the case of a Newtonian fluid. Also, the more significant the shear-thinning nature of a fluid is, the larger the $|\mu^*|$. These are consistent with those of the previous studies where a boundary was uncharged.^{25–30} Note that if $\mu^* < 0$, μ^* is more sensitive to the variation in $(\alpha U/a)$ than that in n , which has not been reported previously.

3.2. Positively Charged Sphere in a Positively Charged Cavity. Let us consider next the case in which both a sphere and a cavity are positively charged. Note that because the present problem is of nonlinear nature, the electrophoretic mobility in this case cannot be obtained directly by a linear combination of the mobility in the previous section and the mobility for the case in which a positively charged sphere is in an uncharged cavity.

Figure 7. Contours of the scaled viscosity η^* for a Carreau fluid with $n = 0.8$ and $\alpha U/a = 0.8$ for the case of Figure 6 at $P = 60\%$: (a) $ka = 0.1$; (b) $ka = 1$; (c) $ka = 2$; and (d) $ka = 5$.

Figure 8. Variation of the scaled electrophoretic mobility μ^* as a function of the position parameter P for various $(\alpha U/a)$ values at $n = 0.8$ and $\lambda = 0.4$ (a) and that at various n values at $\alpha U/a = 0.2$ (b). Key: $\zeta_p^* = 0$, $\zeta_w^* = 1$, and $ka = 1$.

The influences of the position parameter P and the relative size of a sphere λ ($= a/b$) on the scaled mobility μ^* are illustrated in Figure 10; the results for the corresponding Newtonian fluid are also presented for comparison. For both Newtonian and Carreau fluids, μ^* is seen to be always positive. This is because the net electric force acting on a sphere is always positive for the present case. A comparison between Figures 2b and 10a reveals that μ^* declines faster as P or λ increases in the present case than in the case of a charged particle in an uncharged cavity.

This arises from the dependence of the effect of viscous retardation due to the presence of a cavity, and the negative charge induced on the sphere surface on the variations of P and λ . Figures 2b and 10a also indicate that if the boundary effect is unimportant (λ is small) and P is not too large, for both Newtonian and Carreau fluids, μ^* for the case in which both a sphere and a cavity are positively charged is greater than that for the case in which a positively charged sphere is in an uncharged cavity; however, the reverse is true if λ and/or P are large. This was not observed

Figure 9. Variation of the scaled electrophoretic mobility μ^* as a function of κa for various $(\alpha U/a)$ values at $n = 0.8$ and $P = 90\%$ (a) and that at various n values at $\alpha U/a = 0.2$ (b). Key: same as that in Figure 6.

Figure 10. Variation of the scaled electrophoretic mobility μ^* as a function of the position parameter P at various λ values (a) and as a function of λ at various P values (b). Solid curves represent results for a Newtonian fluid and dashed curves represent results for a Carreau fluid with $n = 0.8$ and $\alpha U/a = 0.8$. Key: $\zeta_p^* = 1$, $\zeta_w^* = 1$, and $\kappa a = 1$.

by Lee et al.⁴ in a study of the electrophoresis of a sphere at the center of a spherical cavity, which was filled with a Newtonian fluid. The former is because the electroosmotic flow induced by the charged cavity, which is in the same direction as that of the applied electric field, is fast if λ and/or P are small. The latter is because the amount of negative charge induced on the sphere surface becomes large if λ and/or P are large.

The influences of the position parameter P and the thickness of double layer κa on the behavior of the scaled mobility μ^* are illustrated in Figure 11. For comparison, the results for the corresponding Newtonian fluid are also presented. For both Newtonian and Carreau fluids, μ^* is always positive and increases monotonically with the increase in κa . However, μ^* is more sensitive to the variation of κa for a Carreau fluid than that for the corresponding Newtonian fluid. For fixed κa and P , μ^* (Newtonian) is smaller than μ^* (Carreau), and the difference between the two increases with the increase in κa , which is consistent with the observation of Lee et al.,²⁵ where a charged sphere is at the center of an uncharged spherical cavity. Note that if κa is small, the difference [μ^* (Carreau) - μ^* (Newtonian)] for the present case is smaller than that for the case in which a positively charged sphere is in an uncharged cavity;^{25,26} however, the reverse is true if κa is large. These arise from the behaviors of the forces acting on a sphere as κa varies. The electric force acting on a sphere is positive (so is μ^*), and it increases with the

increase in κa . The force acting on a sphere arising from the recirculation electroosmotic flow, which is in the same direction as that of the electric force, also increases with the increases in κa . If κa is small, the amount of negative charge induced on the sphere surface due to the presence of the positively charged cavity, which has the effect of decreasing the net electric force acting on the sphere, is large. Also, because the recirculation electroosmotic flow is slow at the same time, the value of μ^* is smaller than that for the case in which a positively charged sphere is in an uncharged cavity.^{25,26} The situation becomes reversed if κa is large, namely the value of μ^* for the case in which a positively charged sphere is in a positively charged cavity becomes larger than that for the case in which a positively charged sphere is in an uncharged cavity. Since the larger the κa , the greater the forces acting on a sphere, the larger the μ^* , the greater the shear rate, and the more significant the effect of shear-thinning, we conclude that if κa is large, the effect of shear-thinning for the case in which both a sphere and a cavity are positively charged is more important than that for the case in which a sphere is positively charged and a cavity is uncharged,^{25,26} but the reverse is true if κa is small. It is interesting to note that the value of κa at which the difference [μ^* (Carreau) - μ^* (Newtonian)] for the case in which both a sphere and a cavity are positively charged becomes larger than that for the case in which a positively charged sphere is in an uncharged cavity increases with the increase in

Figure 11. Variation of the scaled electrophoretic mobility μ^* as a function of the position parameter P at various κa values (a) and as a function of κa at various P values (b). Solid curves represent results for a Newtonian fluid and dashed curves represent results for a Carreau fluid with $n = 0.8$ and $\alpha U/a = 0.8$. Key: $\zeta_p^* = 1$, $\zeta_w^* = 1$, and $\lambda = 0.4$.

Figure 12. Variation of the scaled electrophoretic mobility μ^* as a function of the position parameter P for various $(\alpha U/a)$ values at $n = 0.8$ and $\lambda = 0.4$ (a) and that at various n values at $\alpha U/a = 0.2$ (b). Key: same as that in Figure 10.

Figure 13. Variation of the scaled electrophoretic mobility μ^* as a function of κa for various $(\alpha U/a)$ values at $n = 0.8$ and $P = 90\%$ (a) and that at various n values at $\alpha U/a = 0.2$ (b). Key: same as that in Figure 11.

P . This is because if κa is small, the larger the P , the more significant the influence of the negative charge induced on the sphere surface.

The influence of the nature of a Carreau fluid on the scaled electrophoretic mobility of a sphere μ^* is illustrated in Figures 12 and 13. The qualitative behaviors of μ^* observed in these

figures are similar to those observed for the case of a Newtonian fluid. In general, the more significant the effect of shear-thinning, that is, a larger $(\alpha U/a)$ and/or a smaller n , the larger the μ^* , and the larger the P and/or the smaller the κa , the smaller the μ^* . These are expected and can be explained by reasoning similar to that employed in the discussion of Figures 8 and 9.

4. Conclusions

The influence of a charged boundary on the electrophoretic behavior of a particle in a non-Newtonian fluid is investigated by considering a sphere at an arbitrary position in a spherical cavity filled with a Carreau fluid. The results of numerical simulations reveal that the presence of a charged boundary yields an electroosmotic flow, which makes the electrophoretic behavior of a particle much more complicated than that for the case when the boundary is uncharged. We show that the mobility of a sphere depends mainly upon four factors, namely the position and the relative size of a sphere, the thickness of a double layer, and the nature of a fluid. The shear-thinning effect is found to correlate positively with the boundary effect. Also, this effect is important if the double layer is either sufficiently thin or sufficiently thick. For the case in which an uncharged sphere is placed in a positively charged cavity, if the relative size of a sphere, measured by λ , is large or the thickness of a double layer, measured by κa , is small (thick double layer), the mobility, represented by μ^* , is negative and $|\mu^*|$ declines monotonically with the increase in the deviation of a sphere from the center of a cavity, measured by P . If λ or κa takes a medium value, $|\mu^*|$ has a local maximum as P varies. If λ is small and/or κa is large (thin double layer),

μ^* changes its sign from positive to negative as P increases and $|\mu^*|$ has a local maximum. However, if κa is sufficiently large, then μ^* is positive and declines with the increase in P . If the boundary effect is important (λ and/or P are large), then $\mu^* < 0$; on the other hand, if it is unimportant, μ^* changes its sign from positive to negative as λ and/or P increase. For a fixed P , μ^* changes its sign from negative to positive as κa increases. For the case where both a sphere and a cavity are positively charged, μ^* is always positive. If the boundary effect is unimportant and/or the double layer is thin, μ^* in the present case is greater than that for the case when a positively charged sphere is in an uncharged cavity; however, the reverse is true if the boundary effect is important and/or the double layer is thick. μ^* is more sensitive to the variation in κa for a Carreau fluid than that for the corresponding Newtonian fluid. If κa is large, the effect of shear-thinning in the present case is more important than that for the case when a positively charged sphere is in an uncharged cavity, but the reverse is true if κa is small.

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