

Electrophoresis of dielectric and immiscible-liquid-layer-encapsulated colloids in aqueous mediaBinod Kumar,¹ Simanta De,² Partha P. Gopmandal^{3,*}, R. K. Sinha,¹ and H. Ohshima⁴¹*Department of Mathematics, National Institute of Technology Patna, Patna-800005, India*²*Department of Mathematics, University of Gour Banga, Malda-732103, India*³*Department of Mathematics, National Institute of Technology Durgapur, Durgapur-713209, India*⁴*Faculty of Pharmaceutical Sciences, Tokyo University of Science, Noda, Chiba, Japan*

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In this paper we consider the electrophoresis of a functionalized nanoparticle in electrolyte solution. The undertaken particle is comprised of a rigid inner core encapsulated with a layer of dielectric liquid (e.g., oil or lipid layer), which is immiscible to the bulk aqueous medium. The peripheral liquid layer of the undertaken nanoparticle contains mobile charges due to presence of solubilized surfactants. The mobile electrolyte ions can penetrate across the peripheral layer depending on the difference in the Born energy of the both phases. Such types of nanoparticles have received substantial attention due to their widespread applications in biomedical research. The electric double layer (EDL) is governed by the linearized Poisson-Boltzmann equation under a low potential limit and the electroosmotic flow field is governed by modified Stokes equation. We adopt the flat-plate formalism to obtain the closed analytical expression for the electrophoretic mobility of the undertaken particle under a thin EDL approximation. The dependence of electrophoretic mobility on the pertinent parameters is also illustrated.

DOI: [10.1103/PhysRevE.102.042618](https://doi.org/10.1103/PhysRevE.102.042618)**I. INTRODUCTION**

When a charged colloid is in contact with an electrolyte solution, a layer of mobile ions bearing net nonzero charge may form near the charged surface. Such a layer, often termed as electric double layer (EDL) plays an important role on the electrokinetics of the colloids [1–3]. The study of the electrokinetic transport of colloidal particles, especially the electrophoresis, is one of the convenient tools to measure the electric properties of the colloid from the electrophoretic mobility data (i.e., electrophoretic velocity per unit field strength) [4,5]. A huge body of literature on the electrophoresis of rigid colloid is available due to widespread applications in numerous fields including biological, biomedical, biochemical, environmental sciences, etc. [6–16].

It may be noted that the functionalized nanoparticles find their widespread applications in drug delivery [17–19]. Li *et al.* [20] present a review article on the recent progress of the applications of nanoparticles as the controlled drug carrier. It may be noted that the nanoparticle used as drug carrier, where the drug material can either be absorbed along the surface of the nanocarrier or it may be enveloped by the particles. Such functionalized nanoparticles are suitable for biomedical applications due to controlled-release, site-specific delivery of the encapsulated drug and a long circulation time in the body, etc. [21]. The widely used functionalized nanoparticles for drug delivery are classical micelles, dendrimers, etc., which can be viewed as a composite core-shell soft particle comprised of inner core grafted with polymeric shell [22]. A series of

theoretical and experimental studies on the electrophoresis of such types of nanoparticles are made by several researchers [4,23–33].

Besides the gigantic development of the studies on electrokinetics of soft layer encapsulated nanoparticles, there are also various experimental works on the lipid layer encapsulated nanoparticles. Such type of particles has also proven to be highly efficient as the carrier for targeted drug delivery system [34–37]. In addition, the lipid layer encapsulated nanoparticles are also advantageous to carry the multiple cargos with various chemical combinations, however, a little attention is paid in theoretical modeling to study the electrokinetic behavior of such types of nanocarriers. One of the early work in this direction was made by Mauro [38] to calculate the Donnan potential of a charged membrane that entraps additional immobile ions and allows the penetration of mobile electrolyte ions. However, such a model cannot be used for a lipid membrane in which the lipid molecules are distributed according to the equilibrium law, i.e., Boltzmann distribution. Later, Ohshima *et al.* [39] present a theoretical model, to calculate the electrostatic potential of a lipid membrane containing additional mobile charges due to lipid molecules.

It may be noted that for a cell membrane, oil layer, or lipid layer coated colloidal particle, the electrostatic behavior differs significantly than that of the rigid colloids. Here the liquid in peripheral layer and the bulk electrolyte solution are completely insoluble in each other (i.e., immiscible), which results in various two-phase electrostatic phenomena [40]. In addition, the difference in dielectric permittivity of the peripheral layer of the immiscible liquid and electrolyte solution may lead to the difference in Born energy of both the phases, which further lead to the significant ion partitioning effect

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[41]. A number of research papers are available on the electrohydrodynamics of two-phase flow through the microfluidic devices under various electrostatic conditions [42,43]. However, in all these papers the electrohydrodynamics are studied inside a narrow confinement and are not directly applicable for the electrokinetic behavior of cell membrane, oil layer, or lipid layer coated colloidal particles.

In this paper we have presented a theoretical model for the electrophoresis of a composite nanoparticle in extent of an aqueous medium. The particle is comprised of rigid inner core encapsulated with a layer of dielectric and immiscible liquid (e.g., oil or lipid layer). The peripheral layer allows the penetration of mobile ions from the bulk aqueous media through a discontinuous manner as a consequence of ion partitioning effect induced due to the difference in dielectric permittivity of both the phases. Furthermore, additional mobile charges may also present along the peripheral liquid layer due to presence of solubilized surfactants, which is possible when the peripheral liquid layer bears ions adsorbed with surfactant molecules, e.g., cationic peptides or anionic AOT. There are many examples of lipid layer coated particles, which are often called lipoparticles [44,45]. In the field of drug delivery systems (DDS), in particular, cell membrane coated nanoparticles have been extensively used. According to the Singer-Nicolson fluid mosaic membrane model [46], biological membranes are two-dimensional viscous lipid bilayers in which lipid and protein molecules are free to move laterally. The theory presented in this paper can be applied to these systems. Our model is based on the classical flat-plate formulation, which is, however, often considered for electrophoresis of biocolloids [47–52]. In the present study, we derive an explicit analytical expression of electrophoretic mobility by incorporating the appropriate interfacial boundary conditions for electrostatic potential and fluid velocity.

II. MATHEMATICAL MODEL

In the present study we consider the electrophoresis of a composite nanoparticle comprised of rigid inner core surrounded by a layer of dielectric liquid of thickness δ . The liquid in peripheral layer is immiscible to the bulk aqueous medium. The problem is studied in the limit where the EDL thickness is far smaller than the particle size. Such a situation is often met for the particle electrophoresis in electrolyte medium with sufficiently high electrolyte concentration and we may adopt the flat-plate theory to study the problem. The particle is dispersed in a binary symmetric $z : z$ electrolyte medium with bulk molar concentration n_0 . The applied electric field of strength E is set parallel to the particle surface. We fix the x axis perpendicular to the surface of the particle and the origin is located at the interface of the peripheral liquid layer and aqueous medium. A schematic diagram of the present situation viewed in the flat-plate representation is shown in Fig. 1.

The surface of the inner rigid core is considered to be hydrophilic and electrically neutral. The peripheral dielectric and immiscible liquid layer may bear additional mobile charges, e.g., absorbed ions or the solubilized surfactants. Without loss of generality we consider its valence as $-Z$. The bulk molar concentration of the additional mobile ions

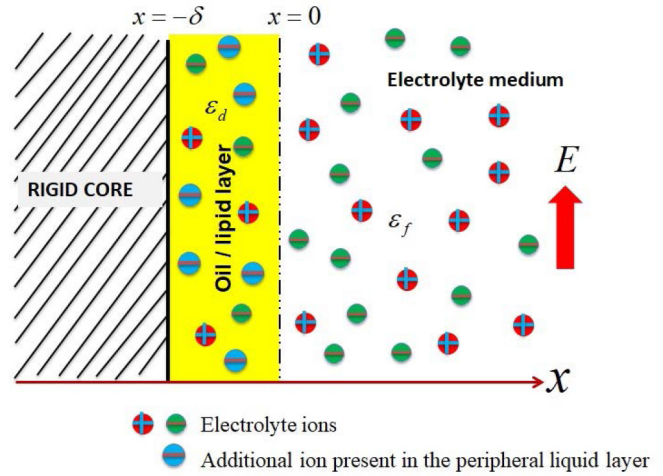


FIG. 1. Schematic illustration of platelike composite particle comprised of inner rigid core coated with a layer of immiscible liquid of thickness δ . The electric field of strength E is applied parallel to the surface of the particle.

within the layer of immiscible liquid is considered to be N_0 and its subsistence in electrolyte medium is considerably less compared to the electrolyte and hence, we may assume that the additional mobile charges are present only in the peripheral layer [39,42]. Further, the surfactant molecules present in peripheral layer may give rise to a fixed charge density (σ) at the interface of the adjacent liquids. Below we have provided the description of the electrostatic potential distribution, electroosmotic flow field and subsequently we have presented the detailed derivation of the closed form expression for the electrophoretic mobility.

A. Electrostatic potential

The potential distribution for the undertaken problem is determined from the Poisson-Boltzmann equation relating the electrostatic potential $\phi(x)$ and the net charge density due to mobile ions, given as

$$-\varepsilon_d \frac{d^2 \phi}{dx^2} = \rho_d(x), \quad -\delta < x < 0; \quad (1a)$$

$$-\varepsilon_e \frac{d^2 \phi}{dx^2} = \rho_e(x), \quad 0 < x < \infty. \quad (1b)$$

Here ε_d and ε_e are the permittivities of the immiscible liquid layer and electrolyte media, respectively. The net charge densities at a position x within the peripheral layer and electrolyte medium are denoted by $\rho_d(x)$ and $\rho_e(x)$, respectively, and are defined as

$$\rho_d(x) = F[z n_+(x) - z n_-(x) - Z n_d(x)], \quad -\delta < x < 0; \quad (2a)$$

$$\rho_e(x) = F[z n_+(x) - z n_-(x)], \quad 0 < x < \infty. \quad (2b)$$

Here F is the Faraday constant, $n_{\pm}(x)$ are the concentration (in mM) of cations and anions of the background electrolyte and $n_d(x)$ is the concentration (in mM) of the additional

negative charge present in the peripheral layer at a given position x .

Under a low potential limit we assume that both the electrolyte ions present within and outside the oil layer (i.e., for $0 < x < \infty$) and additional mobile ions present within the surface layer ($-\delta < x < 0$), follows the Boltzmann distribution, given as

$$\left. \begin{aligned} n_{\pm}(x) &= bn_0 \exp\left(\mp \frac{zF\phi(x)}{RT}\right) \\ n_d(x) &= BN_0 \exp\left(\frac{ZF\phi(x)}{RT}\right) \end{aligned} \right\} \quad -\delta < x < 0 \quad (3a)$$

$$\left. \begin{aligned} n_{\pm}(x) &= n_0 \exp\left(\mp \frac{zF\phi(x)}{RT}\right) \\ n_d(x) &= 0 \end{aligned} \right\} \quad 0 < x < \infty. \quad (3b)$$

Here R is the gas constant and T is absolute temperature. The constant b appearing in the first equation of (3) represents the ion partition coefficient, defined as [53]

$$b = \exp\left(-\frac{\Delta W}{k_B T}\right), \quad (4)$$

where k_B is Boltzmann constant. The difference in Born energy, denoted by ΔW represents the difference of the electrostatic energy of mobile electrolyte ions in the immiscible liquid layer and aqueous media, is defined as [54]

$$\Delta W = \frac{(ze)^2}{8\pi r} \left\{ \frac{1}{\varepsilon_d} - \frac{1}{\varepsilon_e} \right\}. \quad (5)$$

Here e is the elementary charge and r is the radius of mobile electrolyte ions, taken to be same ($= 3.3 \text{ \AA}$) for both the cation and anion [54]. It may be noted that the difference in Born energy always opposes the movement of mobile ions from high to low dielectric media. Reduction in the difference between dielectric permittivity of the adjacent liquid layer and bulk electrolyte phase reduces the corresponding difference in Born energy. In fact, the penetration of the solvent molecules inside the oil layer is controlled by the ion partition coefficient b , which satisfies the typical condition for ion concentration (n_{\pm}) at the interface ($x = 0$), given by $n_{\pm}(0^-) = bn_{\pm}(0^+)$.

The constant B appearing in the second equation of (3) denotes the normalization factor, which can be obtained from the relation given below

$$\int_{-\delta}^0 n_d(x) dx = N_0 \delta.$$

Using the expression for $n_d(x)$ into the above equation we may easily deduce the value of B , given as

$$B = \frac{\delta}{\int_{-\delta}^0 \exp\left(\frac{ZF\phi(x)}{RT}\right) dx}. \quad (6)$$

We denote the Donnan potential (the value of the electrostatic potential deep inside the immiscible liquid layer) by ϕ_D . If the thickness of the peripheral liquid layer δ is much greater than the Debye length κ^{-1} (i.e., $\kappa\delta \gg 1$), then the EDL potential $\phi(x)$ is approximately equals to ϕ_D for most of the part in the region $-\delta < x < 0$. In such a case, we can calculate the value

of B as $B = \exp(-ZF\phi_D/RT)$. Proceeding the way as discussed by Ohshima *et al.* [39], one can easily obtain the value of Donnan potential as $\phi_D = -(RT/zF) \sinh^{-1}(ZN_0/2bz n_0)$.

In order to find the solution of potential equation, we apply the Debye-Hückel linearization. Such an approximation is, however, valid if the EDL potential is lower than the thermal voltage drop, i.e., $\phi < \phi_0 (= RT/zF)$. Hence we may write the linearized form of the Poisson-Boltzmann equation as follows:

$$\frac{d^2\phi}{dx^2} = \kappa_1^2 \phi + Q, \quad -\delta < x < 0; \quad (7a)$$

$$\frac{d^2\phi}{dx^2} = \kappa^2 \phi, \quad 0 < x < \infty, \quad (7b)$$

where $\kappa = \sqrt{2zFn_0/\varepsilon_e\phi_0}$, $\kappa_1 = \sqrt{\kappa^2(b\varepsilon_e/\varepsilon_d) + (Q/\phi_0)}$ and $Q = ZFN_0B/\varepsilon_d$. Equations (7) need to be solved subject to the following boundary conditions:

$$\left. \frac{d\phi}{dx} \right|_{x=-\delta} = 0, \quad (8a)$$

$$\varepsilon_d \left. \frac{d\phi}{dx} \right|_{x=0^-} - \varepsilon_e \left. \frac{d\phi}{dx} \right|_{x=0^+} = \sigma, \quad (8b)$$

$$\left. \phi \right|_{x=0^-} = \left. \phi \right|_{x=0^+}, \quad (8c)$$

$$\phi \rightarrow 0 \quad \text{as } x \rightarrow \infty. \quad (8d)$$

The condition presented in Eq. (8a) is due to electrically neutral inner rigid core surface of the particle. Equations (8b) and (8c) represent the continuity of displacement vector and potential across the immiscible liquid layer and electrolyte interface, respectively. In addition along the far field (i.e., $x \rightarrow \infty$), the EDL potential gradually approaches to its bulk value (zero potential). Using the conditions given in Eq. (8), the solution of Eq. (7) may be written as

$$\phi(x) = \begin{cases} L_1 \exp(\kappa_1 x) + L_2 \exp(-\kappa_1 x) - \frac{Q}{\kappa_1^2} & -\delta \leq x \leq 0; \\ L_3 \exp(-\kappa x) & 0 \leq x < \infty, \end{cases} \quad (9)$$

where the coefficients L_i ($i = 1, 2, 3$) are given below

$$\left. \begin{aligned} L_1 &= L_2 \exp(2\kappa_1 \delta), \\ L_2 &= \frac{L_3 + Q/\kappa_1^2}{1 + \exp(2\kappa_1 \delta)}, \\ L_3 &= \frac{\sigma - \varepsilon_d \tanh(\kappa_1 \delta) Q / \kappa_1}{\varepsilon_d \kappa_1 \tanh(\kappa_1 \delta) + \varepsilon_e \kappa} \end{aligned} \right\}. \quad (10)$$

B. Electroosmotic flow field and electrophoretic mobility

The governing equations for the steady flow within low Reynolds number regime are described by the Stokes equation, given as

$$\mu_d \frac{d^2 u}{dx^2} + \rho_d(x) E = 0, \quad -d < x < 0; \quad (11a)$$

$$\mu_e \frac{d^2 u}{dx^2} + \rho_e(x) E = 0, \quad 0 < x < \infty, \quad (11b)$$

where μ_d and μ_e are the viscosity of the immiscible liquid layer and electrolyte medium, respectively. Using the explicit form of the $\rho_d(x)$ and $\rho_e(x)$ provided earlier, the reduced form of the fluid flow equations may be written as

$$\mu_d \frac{d^2 u}{dx^2} - \varepsilon_d E \frac{d^2 \phi}{dx^2} = 0, \quad -\delta < x < 0; \quad (12a)$$

$$\mu_e \frac{d^2 u}{dx^2} - \varepsilon_e E \frac{d^2 \phi}{dx^2} = 0, \quad 0 < x < \infty. \quad (12b)$$

The respective boundary conditions considered for the velocity along the inner core surface ($x = -\delta$), interface between immiscible liquid layer and electrolyte medium ($x = 0$) and along the far field ($x \rightarrow \infty$) are

given below

$$u \Big|_{x=-\delta} = 0, \quad (13a)$$

$$\mu_d \frac{du}{dx} \Big|_{x=0^-} - \mu_e \frac{du}{dx} \Big|_{x=0^+} = \sigma E, \quad (13b)$$

$$u \Big|_{x=0^-} = u \Big|_{x=0^+}, \quad (13c)$$

$$u \rightarrow -U_E \quad \text{as } x \rightarrow \infty, \quad (13d)$$

where U_E is the electrophoretic velocity of the particle. Here we adopt the EDL plus surface charge model to incorporate the boundary conditions along the interface [55]. By solving equations (12) subject to boundary conditions (13) we may obtain the electroosmotic flow field as follows:

$$u(x) = \begin{cases} \frac{\varepsilon_d E}{\mu_d} [\phi(x) - \phi(-\delta)], & -\delta \leq x \leq 0; \\ \frac{\varepsilon_e E}{\mu_e} [\phi(x) - \phi(0)] + \frac{\varepsilon_d E}{\mu_d} [\phi(0) - \phi(-\delta)], & 0 \leq x < \infty, \end{cases} \quad (14)$$

where $\phi(0) = L_3$ and $\phi(-\delta) = 2L_2 \exp(\kappa_1 \delta) - Q/\kappa_1^2$, are the induced potential at the immiscible liquid layer electrolyte interface and surface of the inner rigid core, respectively.

The general expression for the electrophoretic mobility can be obtained from the following relation:

$$\bar{\mu}_E = U_E/E = - \lim_{x \rightarrow \infty} u(x)/E. \quad (15)$$

Using the derived expression (14) for $u(x)$ we may write

$$\bar{\mu}_E = \frac{\varepsilon_e}{\mu_e} \phi(0) - \frac{\varepsilon_d}{\mu_d} [\phi(0) - \phi(-\delta)]. \quad (16)$$

Substituting the values of $\phi(0)$ and $\phi(-\delta)$ in Eq. (16), we may derive the closed form expression for the electrophoretic mobility of the undertaken particle, given as

$$\bar{\mu}_E = \left[\frac{\varepsilon_e}{\mu_e} + \frac{\varepsilon_d}{\mu_d} \left(\frac{1}{\cosh(\kappa_1 \delta)} - 1 \right) \right] \left(\frac{\sigma - \varepsilon_d \tanh(\kappa_1 \delta) \frac{Q}{\kappa_1}}{\varepsilon_d \kappa_1 \tanh(\kappa_1 \delta) + \varepsilon_e \kappa} \right) + \frac{\varepsilon_d}{\mu_d} \left[\frac{1}{\cosh(\kappa_1 \delta)} - 1 \right] \frac{Q}{\kappa_1^2}. \quad (17)$$

Equation (17) can be used for fitting electrophoretic mobility data measured on particles in the limit where the EDL thickness is far smaller than the particle size upon adjustment of the charge density across the peripheral liquid layer and along the liquid-liquid interface, the dielectric permittivity and viscosity of the peripheral liquid layer and electrolyte solution.

For a composite colloid coated with reasonably thick surface layer of dielectric and immiscible liquid, the mobility expression may be approximated as

$$\bar{\mu}_E = \left(\frac{\varepsilon_e}{\mu_e} - \frac{\varepsilon_d}{\mu_d} \right) \left(\frac{\sigma - \varepsilon_d \frac{Q}{\kappa_1}}{\varepsilon_d \kappa_1 + \varepsilon_e \kappa} \right) - \frac{\varepsilon_d}{\mu_d} \frac{Q}{\kappa_1^2}. \quad (18)$$

In the limit $\varepsilon_d \approx \varepsilon_e$ (i.e., in the absence of ion partitioning effect) the mobility expression (17) further reduces to

reduces to

$$\bar{\mu}_E = \left[\frac{1}{\mu_e} + \frac{1}{\mu_d} \left(\frac{1}{\cosh(\tilde{\kappa} \delta)} - 1 \right) \right] \left(\frac{\sigma - \varepsilon_d \tanh(\tilde{\kappa} \delta) \frac{Q}{\tilde{\kappa}}}{\tilde{\kappa} \tanh(\tilde{\kappa} \delta) + \kappa} \right) + \frac{\varepsilon_d}{\mu_d} \left[\frac{1}{\cosh(\tilde{\kappa} \delta)} - 1 \right] \frac{Q}{\tilde{\kappa}^2}, \quad (19)$$

where $\tilde{\kappa} = \sqrt{\kappa^2 + Q/\phi_0}$.

III. COMPUTATIONAL ILLUSTRATIONS

In this section we have discussed the dependence of the calculated mobility on the pertinent parameters. To illustrate, we have presented the scaled mobility μ_E , scaled by $\mu_0 (= \varepsilon_e \phi_0 / \eta)$. For computing the electrophoretic mobility, the thickness of the immiscible liquid layer is considered to be of the order of 10 nm. The dielectric constant and the viscosity of the aqueous medium are taken to be 80 and 1 mPa·s, respectively. Unless stated otherwise, we consider the dielectric immiscible liquid as oily organic solvent cyclohexyl bromide (CHB) with dielectric constant as 7.9 and viscosity 2.269 mPa·s, respectively [56]. In addition, we have also shown the results by varying the dielectric permittivity and viscosity of the surface layer of immiscible liquid. The concentration of the negative mobile charge present within the surface layer (N_0) is varied from 0.1–100 mM. The electrolyte concentration is considered to be high enough ($n_0 = 10^2$ mM) so that the EDL thickness ($\kappa^{-1} \sim 1$ nm) is much smaller than the particle size. It may be noted that for particle electrophoresis, if the concentration of bulk electrolyte is higher than 1 mM and outer layer charge is lower than 100 mM, the relaxation effect is almost negligible [57]. The surface charge density (σ) along the interface ($x = 0$) is given by $\sigma = -e/S$, where S represents the area per free charged molecule in the peripheral layer present along the interface. Ohshima *et al.* [39] suggested that the value of σ can be varied either by varying S introducing experimentally the neutral lipids of by

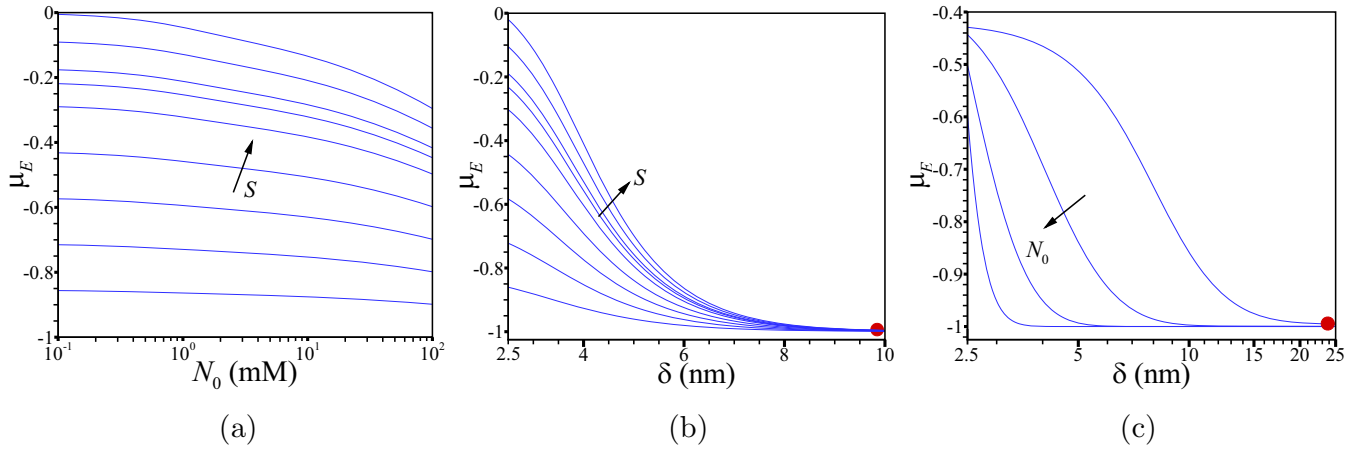


FIG. 2. Variation in the scaled mobility (μ_E) with the (a) concentration of additional mobile ion within immiscible liquid layer for fixed $\delta = 5$ nm; (b) thickness of immiscible liquid layer for fixed $N_0 = 1$ mM. The results are presented in (a) and (b) for various combinations of $S (= 1000, 1200, 1500, 2000, 3000, 4000, 5000, 10000, \infty \text{ \AA}^2)$; In (c) we have shown the variation in the scaled mobility with the thickness of the immiscible liquid layer (δ) for fixed $S = 1000 \text{ \AA}^2$ and different choices of $N_0 (= 0.1, 1, 10, 100 \text{ mM})$. The symbol in (b), (c) represents the limiting situation under sufficiently thick immiscible liquid layer (i.e., $\delta \rightarrow \infty$), given in Eq. (18).

regulating bulk pH of the aqueous media. It may be noted that $S \rightarrow \infty$ corresponds the uncharged interface.

In Fig. 2, we presents the results for the scaled electrophoretic mobility of an encapsulated colloidal particle, coated with a layer of oily CHB solvent. In Fig. 2(a), we have shown the scaled mobility as a function of the concentration N_0 of the additional mobile ions present along the peripheral layer. The results are presented for various choices of interfacial surface charge σ , where σ is varied by varying the value of S . Figure 2(a) indicates that the magnitude in the mobility increases for increase in concentration of the additional mobile ions across the peripheral liquid layer (N_0). Increase in N_0 increases the EDL potential and thereby increases the mobility of the undertaken particle. On the other hand, the mobility reduces with increasing values of S . It is reasonable since the increase in S reduces the interfacial surface charge σ and thereby reduces the electromotive force and hence results in a decrement in electrophoretic mobility. In Figs. 2(b), 2(c) we have shown the variation of scaled mobility with the thickness of the peripheral liquid layer, δ . The results are shown in Fig. 2(b) for various values of S with fixed N_0 and in Fig. 2(c), we have presented the results for fixed value of S with various values of N_0 . As expected, we observe an increment in mobility with the rise in interfacial charge and the concentration of additional mobile ions across the immiscible liquid layer. Increase in δ increases the net charges enclosed in the surface layer, which results in an increment in the mobility.

Figures 2(b) and 2(c) indicate that the magnitude of mobility approaches to the asymptotic plateau value that correctly compares with the predication from Eq. (18) applicable to the nanoparticle encapsulated with a sufficiently thick layer of immiscible liquid. The occurrence of constant mobility with the rise in δ is reasonable, since for such a case the EDL potential within the surface layer is correctly predicted by the constant Donnan potential. As expected, at a given N_0 , the critical choice of δ to achieve the plateau value [i.e., Eq. (18)] is independent of the choice of σ . However, the critical value

of δ reduces with the rise in N_0 . It is reasonable, since for lower value N_0 , the maximum magnitude in mobility may be achieved for thick surface layer and it reduces with the increase in molar concentration of the additional mobile ions distributed across the surface layer of immiscible liquid.

Further in Fig. 3(a) and 3(b) we have illustrated the dependence of electrophoretic mobility on the permittivity ratio $\epsilon_r (= \epsilon_d/\epsilon_f)$ and viscosity ratio $\mu_r (= \mu_d/\mu_f)$ of the peripheral liquid layer to the aqueous media. The result in Fig. 3(a) is shown for fixed value of μ_r by varying the peripheral liquid layer to aqueous media permittivity ratio ϵ_r . Figure 3(a) indicates that the magnitude in mobility decreases with the rise in the value of ϵ_r . The charged dielectric layer of immiscible liquid attracts the counterions and thereby repels the coions. Increase in ϵ_r reduces the effect of ion partitioning and thereby increases the counterions accumulation across the surface layer of immiscible liquid. Hence, the net effective charge enclosed by the peripheral layer reduces, which leads to a reduction in electrophoretic mobility. The results in Fig. 3(b) are shown for fixed value of ϵ_r by varying the peripheral liquid layer to aqueous media viscosity ratio, μ_r . We observed that magnitude in mobility reduces with the increase in μ_r , however, the effect of viscosity ratio is less prominent. For the electrophoresis of undertaken particle is actually regulated by the amount of charges carried by the interface as well as the concentration of the mobile ions distributed across the surface layer of immiscible liquid.

IV. CONCLUSION

We made a parametric study on the electrophoresis of a composite nanoparticle comprised of inner rigid core encapsulated with dielectric layer of immiscible liquid. Based on the flat-plate theory, we derived the closed form expression for the electrophoretic mobility of such a particle under Debye-Hückel approximation. We observed that the interfacial charge and concentration of surfactant molecules distributed across the peripheral layer has a substantial impact

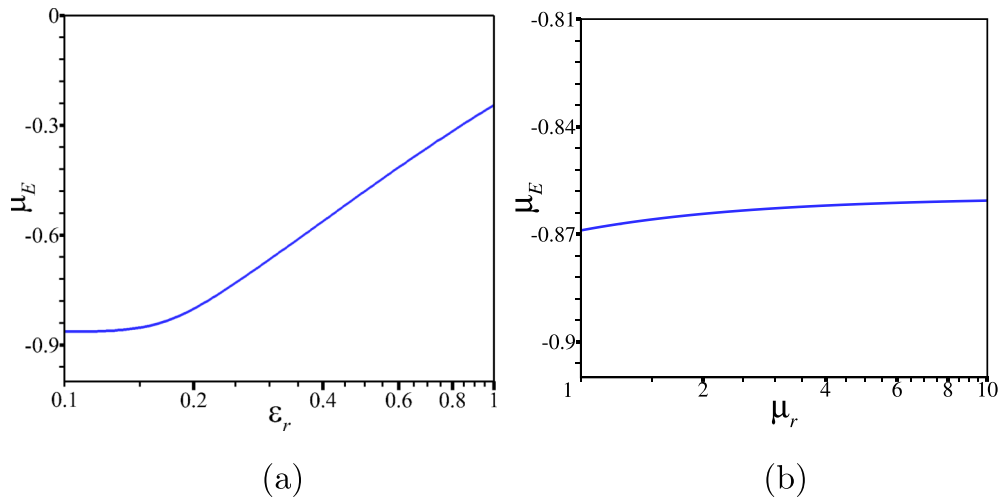


FIG. 3. Variation of the scaled mobility with immiscible liquid layer-to-electrolyte (a) permittivity ratio $\epsilon_r (= \epsilon_d/\epsilon_f)$ for fixed viscosity ratio $\mu_r (= \mu_d/\mu_f = 2.269)$; (b) viscosity ratio (μ_r) with fixed $\epsilon_e = 0.1$. The results are presented here for fixed $\delta = 5$ nm, $N_0 = 1$ mM and $S = 1000 \text{ \AA}^2$.

on the electrophoretic behavior of such type of particle. The effect of permittivity ratio and viscosity ratio of the peripheral liquid layer to the electrolyte solution is also highlighted. We found that the permittivity ratio, which is again related to the ion partitioning effect, has a strong influence on the electrophoretic mobility. However, the impact of viscosity ratio has relatively less impact on the electrophoretic behavior of the undertaken particle, as the EDL-mediated electrostatic potential regulates the motion of the particle.

In this study we have confined ourselves to the thin EDL and low potential case. However, when the EDL is thick or comparable with the particle size and the electric potential

is high, various additional effects such as effect of Debye-Huckel parameter, double-layer polarization, and relaxation effect come into play. Such nonlinear effects are a subject for future research.

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The authors declare that they have no conflict of interest.

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- [1] R. J. Hunter, *Zeta Potential in Colloid Science: Principles and Applications*, Vol. 2 (Academic Press, New York, 2013).
- [2] J. Lyklema, *Fundamentals of Interface and Colloid Science: Solid-Liquid Interfaces*, Vol. II (Academic Press, New York, 1995).
- [3] J. H. Masliyah and S. Bhattacharjee, *Electrokinetic and Colloid Transport Phenomena* (John Wiley & Sons, New York, 2006).
- [4] R. Sonohara, N. Muramatsu, H. Ohshima, and T. Kondo, Difference in surface properties between *Escherichia coli* and *Staphylococcus aureus* as revealed by electrophoretic mobility measurements, *Biophys. Chem.* **55**, 273 (1995).
- [5] J. López-Viota, S. Mandal, A. V. Delgado, J. Toca-Herrera, M. Möller, F. Zanuttin, M. Balestrino, and S. Krol, Electrophoretic characterization of gold nanoparticles functionalized with human serum albumin (HSA) and creatine, *J. Colloid Interface Sci.* **332**, 215 (2009).
- [6] H. Ohshima, T. W. Healy, and L. R. White, Approximate analytic expressions for the electrophoretic mobility of spherical colloidal particles and the conductivity of their dilute suspensions, *J. Chem. Soc. Faraday Trans. 2* **79**, 1613 (1983).
- [7] B. Kumar, P. P. Gopmandal, R. K. Sinha, and H. Ohshima, Electrophoresis of hydrophilic/hydrophobic rigid colloid with effects of relaxation and ion size, *Electrophoresis* **40**, 1282 (2019).
- [8] M. Von Smoluchowski, Elektrische endosmose und stromungsströme, *Handbuch der Elektrizität und des Magnetismus* (Barth, Leipzig, 1921), Vol. 2, p. 366.
- [9] E. Huckel, Die kataphorese der kugel, *Phys. Z.* **25**, 204 (1924).
- [10] D. C. Henry, The cataphoresis of suspended particles. Part I - The equation of cataphoresis, *Proc. R. Soc. Lond. A* **133**, 106 (1931).
- [11] R. W. O'Brien and L. R. White, Electrophoretic mobility of a spherical colloidal particle, *J. Chem. Soc. Faraday Trans. 2* **74**, 1607 (1978).
- [12] J.-P. Hsu and M.-H. Ku, Boundary effect on electrophoresis: finite cylinder in a cylindrical pore, *J. Colloid Interface Sci.* **283**, 592 (2005).
- [13] S. Bhattacharyya and P. P. Gopmandal, Migration of a charged sphere at an arbitrary velocity in an axial electric field, *Colloid Surface A* **390**, 86 (2011).
- [14] A. S. Khair, Strong deformation of the thick electric double layer around a charged particle during sedimentation or electrophoresis, *Langmuir* **34**, 876 (2017).

- [15] S. Stotz, Field dependence of the electrophoretic mobility of particles suspended in low-conductivity liquids, *J. Colloid Interface Sci.* **65**, 118 (1978).
- [16] R. F. Stout and A. S. Khair, A continuum approach to predicting electrophoretic mobility reversals, *J. Fluid Mech.* **752**, R1 (2014).
- [17] T. Sun, Y. S. Zhang, B. Pang, D. C. Hyun, M. Yang, and Y. Xia, Engineered nanoparticles for drug delivery in cancer therapy, *Angew. Chem. Int. Ed.* **53**, 12320 (2014).
- [18] E. Blanco, H. Shen, and M. Ferrari, Principles of nanoparticle design for overcoming biological barriers to drug delivery, *Nature Biotechnol.* **33**, 941 (2015).
- [19] M. Cully, Drug delivery: Nanoparticles improve profile of molecularly targeted cancer drug, *Nature Rev. Drug Discov.* **15**, 231 (2016).
- [20] Q. Li, T. Cai, Y. Huang, X. Xia, S. P. C. Cole, and Y. Cai, A review of the structure, preparation, and application of NLCs, PNPs, and PLNs, *Nanomaterials* **7**, 122 (2017).
- [21] S.-W. Choi, W.-S. Kim, and J.-H. Kim, Surface-functionalized nanoparticles for controlled drug delivery, in *NanoBiotechnology Protocols* (Springer, Berlin, 2005), pp. 121–131.
- [22] J. Callejas-Fernández, J. Estelrich, M. Quesada-Pérez, and J. Forcada, *Soft Nanoparticles for Biomedical Applications*, Nanoscience & Nanotechnology Series (The Royal Society of Chemistry, London, 2014).
- [23] Bharti, P. P. Gopmandal, S. Bhattacharyya, and H. Ohshima, Analytic expression for electrophoretic mobility of soft particles with a hydrophobic inner core at different electrostatic conditions, *Langmuir* **36**, 3201 (2020).
- [24] H. Ohshima, Electrophoretic mobility of a polyelectrolyte-adsorbed particle: Effect of segment density distribution, *J. Colloid Interface Sci.* **185**, 269 (1997).
- [25] H. Ohshima, Electrophoretic mobility of soft particles, *J. Colloid Interface Sci.* **163**, 474 (1994).
- [26] H. Ohshima, Electrophoresis of soft particles, *Adv. Colloid Interface Sci.* **62**, 189 (1995).
- [27] H. Ohshima, Modified henry function for the electrophoretic mobility of a charged spherical colloidal particle covered with an ion-penetrable uncharged polymer layer, *J. Colloid Interface Sci.* **252**, 119 (2002).
- [28] H. Ohshima, Electrophoresis of soft particles: Analytic approximations, *Electrophoresis* **27**, 526 (2006).
- [29] R. J. Hill, D. A. Saville, and W. B. Russel, Electrophoresis of spherical polymer-coated colloidal particles, *J. Colloid Interface Sci.* **258**, 56 (2003).
- [30] J. F. L. Duval, K. J. Wilkinson, H. P. van Leeuwen, and J. Buffle, Humic substances are soft and permeable: Evidence from their electrophoretic mobilities, *Environ. Sci. Technol.* **39**, 6435 (2005).
- [31] U. K. Ghoshal, S. Bhattacharyya, P. P. Gopmandal, and S. De, Nonlinear effects on electrophoresis of a soft particle and sustained solute release, *Transport Porous Med.* **121**, 121 (2018).
- [32] J. Langlet, F. Gaboriaud, C. Gantzer, and J. F. L. Duval, Impact of chemical and structural anisotropy on the electrophoretic mobility of spherical soft multilayer particles: The case of bacteriophage MS2, *Biophys. J.* **94**, 3293 (2008).
- [33] J. F. L. Duval and F. Gaboriaud, Progress in electrohydrodynamics of soft microbial particle interphases, *Curr. Opin. Colloid Interface Sci.* **15**, 184 (2010).
- [34] P. F. Kiser, G. Wilson, and D. Needham, Lipid-coated microgels for the triggered release of doxorubicin, *J. Control. Release* **68**, 9 (2000).
- [35] K. N. J. Burger, R. W. H. M. Staffhorst, H. C. de Vrijlder, M. J. Velinova, P. H. Bomans, P. M. Frederik, and B. de Kruijff, Nanocapsules: Lipid-coated aggregates of cisplatin with high cytotoxicity, *Nat. Med.* **8**, 81 (2002).
- [36] V. Cauda, H. Engelke, A. Sauer, D. Arcizet, J. Radler, and T. Bein, Colchicine-loaded lipid bilayer-coated 50 nm mesoporous nanoparticles efficiently induce microtubule depolymerization upon cell uptake, *Nano Lett.* **10**, 2484 (2010).
- [37] H. Jing and S. Das, Electric double layer electrostatics of lipid-bilayer-encapsulated nanoparticles: Toward a better understanding of protocell electrostatics, *Electrophoresis* **39**, 752 (2018).
- [38] A. Mauro, Space charge regions in fixed charge membranes and the associated property of capacitance, *Biophys. J.* **2**, 179 (1962).
- [39] H. Ohshima, K. Nomura, H. Kamaya, and I. Ueda, Liquid membrane: Equilibrium potential distribution across lipid monolayer-coated oil/water interface, *J. Colloid Interface Sci.* **106**, 470 (1985).
- [40] J. S. H. Lee and D. Li, Electroosmotic flow at a liquid–air interface, *Microfluid. Nanofluid.* **2**, 361 (2006).
- [41] H. G. L. Coster, The double fixed charge membrane: Solution-membrane ion partition effects and membrane potentials, *Biophys. J.* **13**, 133 (1973).
- [42] P. P. Gopmandal and H. Ohshima, Modulation of electroosmotic flow through electrolyte column surrounded by a dielectric oil layer, *Colloid Polym. Sci.* **295**, 1141 (2017).
- [43] Z. Ding, Y. Jian, and W. Tan, Electrokinetic energy conversion of two-layer fluids through nanofluidic channels, *J. Fluid Mech.* **863**, 1062 (2019).
- [44] J. Thevenot, A.-L. Troutier, L. David, T. Delair, and C. Ladavière, Steric stabilization of lipid/polymer particle assemblies by poly (ethylene glycol)-lipids, *Biomacromolecules* **8**, 3651 (2007).
- [45] A.-L. Troutier and C. Ladavière, An overview of lipid membrane supported by colloidal particles, *Adv. Colloid Interface Sci.* **133**, 1 (2007).
- [46] S. J. Singer and G. L. Nicolson, The fluid mosaic model of the structure of cell membranes, *Science* **175**, 720 (1972).
- [47] H. Ohshima and T. Kondo, Electrophoresis of large colloidal particles with surface charge layers. Position of the slipping plane and surface layer thickness, *Colloid Polym. Sci.* **264**, 1080 (1986).
- [48] H. Ohshima and T. Kondo, Electrophoretic mobility and Donnan potential of a large colloidal particle with a surface charge layer, *J. Colloid Interface Sci.* **116**, 305 (1987).
- [49] H. Ohshima and T. Kondo, Approximate analytic expression for the electrophoretic mobility of colloidal particles with surface-charge layers, *J. Colloid Interface Sci.* **130**, 281 (1989).
- [50] H. Ohshima and T. Kondo, On the electrophoretic mobility of biological cells, *Biophys. Chem.* **39**, 191 (1991).
- [51] S. K. Maurya, P. P. Gopmandal, H. Ohshima, and J. F. L. Duval, Electrophoresis of composite soft particles with differentiated core and shell permeabilities to ions and fluid flow, *J. Colloid Interface Sci.* **558**, 280 (2019).

- [52] S. K. Maurya, P. P. Gopmandal, S. Bhattacharyya, and H. Ohshima, Ion partitioning effect on the electrophoresis of a soft particle with hydrophobic core, *Phys. Rev. E* **98**, 023103 (2018).
- [53] J. J. López-García, J. Horno, and C. Grosse, Suspended particles surrounded by an inhomogeneously charged permeable membrane. Solution of the Poisson-Boltzmann equation by means of the network method, *J. Colloid Interface Sci.* **268**, 371 (2003).
- [54] J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic Press, New York, 2015).
- [55] J. S. H. Lee, I. Barbulovic-Nad, Z. Wu, X. Xuan, and D. Li, Electrokinetic flow in a free surface-guided microchannel, *J. Appl. Phys.* **99**, 054905 (2006).
- [56] M. E. Leunissen, J. Zwanikken, R. Van Roij, P. M. Chaikin, and A. Van Blaaderen, Ion partitioning at the oil–water interface as a source of tunable electrostatic effects in emulsions with colloids, *Phys. Chem. Chem. Phys.* **9**, 6405 (2007).
- [57] H. Ohshima, Electrophoretic mobility of a highly charged soft particle: Relaxation effect, *Colloids Surf. A* **376**, 72 (2011).