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An electrokinetic model of drop deformation in an electric field

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An electrokinetic model is proposed to describe a slight drop deformation which is induced by a weak external electric field. The fluids forming the system are considered Newtonian incompressible dielectric liquids containing free electric charge carriers. According to the model, the charge carriers take part in migration, diffusion and convection transport and there is no solute adsorption at the interface. Thermodynamic quasi-equilibrium at the interface is assumed for the charge carriers in the contacting liquids. The interfacial thermodynamic equilibrium is described using a common distribution coefficient for all the carriers. The problem is simplified by assuming equal diffusion coefficients for the different charge carriers within the same liquid. An analytical expression is obtained for slight drop deformation which is proportional to the second power of the applied field strength magnitude. The expression derived represents the drop deformation as a function of the parameters employed in previous theories (O'Konski & Thacher 1953; Allan & Mason 1962; Taylor 1966) as well as two additional parameters. The additional parameters are the ratios of the drop radius to the Debye lengths of the outer and inner liquids, respectively. The expression obtained for the drop deformation is valid for arbitrary values of these parameters. According to the theory prediction, with an increase in the drop radius, the drop deformation monotonically changes from that obtained by O'Konski & Thacher (1953) and Allan & Mason (1962) for perfect dielectric liquids to that obtained by Taylor (1966) for leaky dielectric liquids. Two simplified versions of the general expression are suggested to describe particular cases of a conducting drop in a perfect dielectric liquid and of a perfect dielectric drop in a conducting liquid.

1. Introduction

Under the influence of an applied electric field, a liquid drop surrounded by another liquid changes its shape. This effect has been extensively studied during the past five decades. Much theoretical and experimental effort has been focused on the slight deformation which is observed in relatively weak external fields and is described by rather simple analytical expressions.

It was experimentally found by many authors (O'Konski & Thacher 1953; Taylor

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1964; Garton & Krasucki 1964; Ha & Yang 2000; Lu 2002) that, in sufficiently weak electric fields, the drops elongate along the field strength vector, producing a prolate shaped drop. For some systems, a number of publications (Allan & Mason 1962; Torza, Cox & Mason 1971; Arp, Foister & Mason 1980; Vizika & Saville 1992; Ha & Yang 1995) report drop elongation in the direction perpendicular to the electric field strength, i.e. a oblate shape.

1.1. *Perfect and leaky dielectric models*

Theoretical description of drop deformation in a weak electric field is usually based on two different models which yield two different expressions. They are the perfect and leaky dielectric models.

The perfect dielectric model was employed by O'Konski & Thacher (1953) and Allan & Mason (1962) who independently derived an expression describing the drop deformation. Hereafter, we will refer to this expression as the OTAM result. According to the perfect dielectric model, both the internal and external liquids are assumed to be ideal insulators containing no free charge carriers and, hence, having zero electric conductivity. The force, which deforms a perfect dielectric drop in a perfect dielectric liquid, occurs since the electric field acts on the *bound* polarized electric charges. Under the influence of an electric field, these polarized charges are formed at the interface between two media having different dielectric permitivities. It can be shown that such a force is always normal to the interface. Therefore, in the steady-state regime, this force does not give rise to liquid flows. The stationary deformation of the drop is determined using a balance of the normal stresses which occur due to this force and due to the interfacial tension forces. The interfacial tension force contributes the normal stress balance in the case of a non-zero mean curvature of the interface. The OTAM result always yields the prolate drop shape.

The leaky dielectric model was employed by Taylor (1966) who derived an expression which differs from the OTAM result. Later, a justified version of this expression was published by Melcher & Taylor (1969). We will refer to this expression as Taylor's result. The leaky dielectric model differs from the perfect dielectric model through the assumption of uniform non-zero conductivities of each of the liquids. Thereby, the leaky dielectric model presumes the existence of *free* charge carriers in the liquids. After application of an external electric field, the free charge carriers form the induced free charge at the interface.

The deforming forces, which act normal to the interface, consist of three parts. The first part is the electric force acting on the bound polarized charges which also exists in leaky dielectrics due to a difference in the dielectric permitivities of the liquids. The second part is the electric force acting on the induced charges normal to the interface. Unlike the force acting on the bound polarized charges, the force acting on the induced free charges can have a tangential component, as well. This tangential force acts on the liquid/liquid interface and gives rise to liquid flow inside and outside the drop. At the interface, the liquid flow yields non-zero values of the normal viscous stresses which result in the third part of the deforming force. Taylor (1966) worked out the final balance between these three components and the interfacial tension forces. Finally, Taylor (1966) derived an expression which is capable of predicting both prolate and oblate drop shapes.

Both models yield expressions for the drop deformation which is defined as

$$d = \frac{a_{\parallel} - a_{\perp}}{a_{\parallel} + a_{\perp}}, \tag{1.1}$$

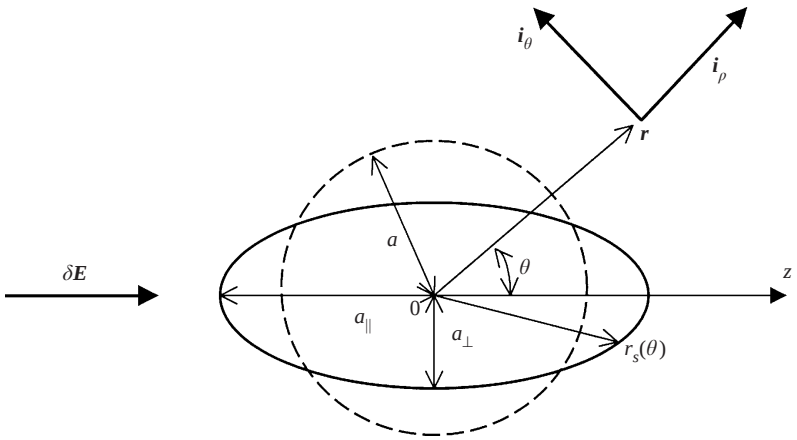

FIGURE 1. A drop in an external electric field, and the spherical coordinate system.

where $a_\parallel$ and $a_\perp$ are the semi-axes parallel and normal to the external field strength (figure 1). For a non-deformed drop $a_\parallel = a_\perp = a$, where a is the drop radius, and $d = 0$. For the prolate shape, $d > 0$, and for the oblate shape, $d < 0$.

The OTAM and Taylor expressions yield a slight drop deformation that corresponds to a sufficiently weak applied field. We will use the notation δ to signify small parameter variations due to applying a weak electric field $\delta \boldsymbol{E}$. For the small drop deformations, δd, both theories give a quadratic dependence, $(\delta E)^2$, which is embedded in the parameter δW:

$$\delta W = \frac{\varepsilon_0 \varepsilon_e a}{\gamma} (\delta E)^2, \tag{1.2}$$

where γ is the interfacial tension coefficient, ε_e is the external liquid dielectric permitivity and ε_0 is the universal dielectric constant.

The OTAM and Taylor expressions differ in the proportionality coefficient between δd and δW, and can be represented respectively as

$$\frac{\delta d_{OTAM}}{\delta W} = \frac{9(S-1)^2}{16(S+2)^2}, \tag{1.3}$$

$$\frac{\delta d_{Taylor}}{\delta W} = \frac{9}{16(H+2)^2} \left[1 + H^2 - 2S + \frac{3}{5}(H-S)\frac{2+3M}{1+M} \right]. \tag{1.4}$$

Both the OTAM result, as $S \to \infty$, and the Taylor result, as $H \to \infty$, approach the common limit given by

$$\frac{\delta d_{common}}{\delta W} = \frac{9}{16}. \tag{1.5}$$

The right-hand side of (1.3) contains one parameter S whereas (1.4) contains three parameters H, S and M. They are the ratios of the internal to external values of the conductivities ($\sigma_{i,e}$), the permitivities ($\varepsilon_{i,e}$) and the viscosities ($\eta_{i,e}$), respectively:

$$S = \frac{\varepsilon_i}{\varepsilon_e}, \quad H = \frac{\sigma_i}{\sigma_e}, \quad M = \frac{\eta_i}{\eta_e}. \tag{1.6}$$

Unlike the original work of Taylor (1966) and some relevant publications by other authors (Torza *et al.* 1971; Vizika & Saville 1992; Saville 1997), each of the definitions given by (1.6) contains the internal coefficient in the numerator and the external in the

denominator. The definitions given by (1.6) make equations (1.3) and (1.4) equivalent to the expressions derived in the original papers (O'Konski & Thacher 1953; Allan & Mason 1962; Taylor 1966; Melcher & Taylor 1969).

It should be noted that, in terms of the ionic concentrations, the range of validity of the two models does not overlap. This follows from the fact that, by using the limiting transition $\sigma_i \to 0$ and $\sigma_e \to 0$ in equation (1.4), one cannot obtain equation (1.3). Strictly speaking, the right-hand side of (1.4) depends on the conductivity ratio, H, and does not depend on the individual conductivities. Therefore, when the ionic concentrations in both liquids approach zero (i.e. $\sigma_i \to 0$ and $\sigma_e \to 0$), while keeping constant the ratio of the ionic concentrations of the different phases (i.e. $H = \sigma_i/\sigma_e = \text{const}$), equation (1.4) is not altered in spite of the fact that both liquids are converted into perfect dielectrics for this transition. Let us consider the physical reasons for this.

Basically, the leaky dielectric model ignores thermal motion of the charge carriers. Accordingly, Taylor (1966) did not take into account the contribution due to diffusion of the charge carriers to the electric current, which means that the local current density, $\boldsymbol{I}$, was represented only by the migration term:

$$\boldsymbol{I} = -\sigma \nabla \Psi, \tag{1.7}$$

where Ψ is the electric potential. Taylor combined equation (1.7) with the steady-state continuity equation for the electric current density

$$\nabla \cdot \boldsymbol{I} = 0. \tag{1.8}$$

For a homogeneous medium ($\sigma = \text{const}$), combining (1.7) and (1.8) leads to the Laplace equation which is written for both the internal and external liquids as

$$\nabla^2 \Psi_{i,e} = 0. \tag{1.9}$$

The Laplace equation (1.9) indicates that free electric charge does not exist in the liquid bulk. At the same time, it can exist at the interface where σ changes sharply. For such an interface, combining (1.7) and (1.8) leads to the boundary condition at the interface

$$(\sigma_e \nabla \Psi_e - \sigma_i \nabla \Psi_i) \cdot \boldsymbol{n} = 0. \tag{1.10}$$

Using (1.10) and the Gauss theorem, one obtains the interfacial charge density, q_S, as

$$q_S = \varepsilon_0 (\varepsilon_e \nabla \Psi_e - \varepsilon_i \nabla \Psi_i) \cdot \boldsymbol{n} = \frac{\varepsilon_0 \varepsilon_e}{\sigma_i} (H - S) \boldsymbol{I} \cdot \boldsymbol{n}. \tag{1.11}$$

where $\boldsymbol{I} = -\sigma_e \nabla \Psi_e$ is the electric current density at the interface. Thus, ignoring the thermal motion of the carriers leads to the consequence that the induced electric charge is entirely localized at the interface within a vanishingly thin layer.

Due to the thermal motion of the charge carriers, the induced charge is expected to be spread out within a region of non-zero dimension. Within such a region, equation (1.7) does not hold and should be corrected by the additional diffusion term. Consequently, the Laplace equation (1.9) should be replaced by the Poisson equation to describe the space electric charge.

To draw a conclusion on whether the leaky dielectric model yields reasonable predictions, one has to assess whether the induced charge layer is sufficiently thin compared with the particle radius, a. The thickness of the free charge layer can be evaluated using the reciprocal Debye parameters for the contacting liquid, $\kappa_{i,e}^{-1}$, (Debye & Huckel 1923). Therefore, it can be expected that a system behaves exactly according

to the leaky dielectric model when $\kappa_{i,e}a \to \infty$. Since the Debye parameter, $\kappa_{i,e}$, is an increasing function of the ionic concentrations (Debye & Huckel 1923), Taylor's result (1.4) is an appropriate approximation for sufficiently high concentrations, i.e. $\kappa_{i,e}a \gg 1$.

The perfect dielectric model, which describes systems with zero ionic concentrations, corresponds to the limiting transition $\kappa_{i,e}a \to 0$. Consequently, the OTAM result (1.3) is an appropriate approximation for systems with sufficiently low ionic concentrations, i.e. $\kappa_{i,e}a \ll 1$. Within the range of intermediate concentrations, which corresponds to $\kappa_{i,e}a = O(1)$, neither Taylor's nor the OTAM theories are valid. Therefore one can expect that these two theories are limiting cases of a more general theory.

1.2. *Electrokinetic model as a 'bridge' between the perfect and leaky dielectric models*

A general theory, which could play the role of a 'bridge' between the OTAM and Taylor results, should be based on the Poisson equation instead of the Laplace equation (1.9). Additionally, the continuity equations should be written for the flux of each of the carriers. Such an equation set is subject to boundary conditions which reflect properties of the interface. Models of this type are referred to as electrokinetic models (Saville 1997).

The need to develop an electrokinetic model for the drop deformation appears to have been first noted by Torza *et al.* (1971). The most general versions of the electrokinetic model were suggested by Baygents & Saville (1991) and Saville (1997). Baygents & Saville (1989) conducted a pioneering analysis to determine how the use of an electrokinetic model can change the expression for the drop deformation, as compared with the Taylor's result given by (1.4). They concluded that, using an electrokinetic model, one cannot obtain any modification to Taylor's expression (1.4). The above conclusion is strictly valid for the limiting case of $\kappa_{i,e}a \to \infty$. This is because of the nature of the approach employed by Baygents & Saville (1989), who used a singular perturbation method in terms of the small parameters $(1/\kappa_{i,e}a)$. They considered the condition $1/\kappa_{i,e}a \ll 1$ since they intended to explain the experiments of Torza *et al.* (1971), which were for relatively large drops with radius of 10^{-3} m.

The objective of the present paper is to derive an analytical expression capable of describing the drop deformation for arbitrary values of the parameters $\kappa_{i,e}a$. In the problem formulation, in contrast with Taylor's model, the contribution of diffusion into ionic transfer will be taken into account and the electric field distribution will be described by the Poisson equation (§ 2). This problem will be solved to obtain the drop deformation (§ 3). Using the limiting transitions of $\kappa_{i,e}a \to 0$ and $\kappa_{i,e}a \to \infty$ in the final expression, we will obtain the drop deformation given by equations (1.3) and (1.4) for the perfect and leaky dielectrics, respectively (§ 4). Combining the limiting transitions of $\kappa_e a \to 0$ and $\kappa_i a \to \infty$ or $\kappa_i a \to 0$ and $\kappa_e a \to \infty$ we will describe the case of a conducting drop in a perfect dielectric liquid or the case of a perfect dielectric drop in a conducting liquid (§ 4).

The electrokinetic theory will be developed using two simplifying assumptions: (i) the drop surface and bulk do not bear any electric charge prior to the electric field being applied; and (ii) the charge carriers have equal diffusion coefficients.

2. Formulation of the mathematical problem

The system under consideration includes a Newtonian liquid drop which is surrounded by another Newtonian liquid. Non-zero conductivity is assumed due to the presence of electric charge carriers in the liquids. In the general case, the concentration of the kth carrier, $C_{i,e}^{(k)}$, changes from point to point.

In the framework of the model, the interface separating the two liquids does not adsorb either the charge carriers or another solute. This assumption, which strictly limits the applicability of the theory, means that the interface does not bear a free electric charge. According to the Gibbs equation, at zero solute adsorption the interface is characterized by a constant value of the interfacial tension coefficient, γ (Adamson & Gast 1997).

The interface is assumed to be vanishingly thin. Therefore, the *local* interfacial thermodynamic equilibrium is established infinitely fast for any external influence. The local thermodynamic equilibrium condition enables one to equate the chemical potentials of the charge carriers in both contacting liquids at the interface. Consequently, one can derive a relationship between the concentrations of the kth carrier in the contacting liquids:

$$\frac{C_i^{(k)}}{C_e^{(k)}} = \alpha^{(k)} \quad \text{at the interface.} \tag{2.1}$$

Here, the distribution coefficient $\alpha^{(k)}$ is assumed to be unaffected by an external influence on the system. This assumption matches with the widely employed Born (1920) model where the distribution coefficient is defined by a difference in the dielectric permitivities of the contacting media and by the ionic radius. Accordingly, for a given charge carrier, the value of $\alpha^{(k)}$ is a constant for given liquids.

2.1. *Thermodynamic equilibrium*

Let us now discuss the actual thermodynamic equilibrium when no external electric field is applied to the system. The equilibrium in a system of two contacting liquids has been considered by many authors. For example, for spherical drops, a relevant analysis can be found in Zholkovskij, Czarnecki & Masliyah (2001). According to this analysis, in the case of zero adsorption the drop bulk bears an equilibrium electric charge if the different charge carriers have different distribution coefficients $\alpha^{(k)}$. The charge and the individual concentrations of the charge carriers are distributed within a certain region of the drop bulk. Consequently, an equilibrium countercharge and relevant concentration distributions are formed outside the drop.

The electric double layer described above does not exist in an equilibrium state when the ions have equal distribution coefficients, i.e.

$$\alpha^{(k)} = \alpha. \tag{2.2}$$

The model studied in the present paper deals with uncharged drops. Thus, the only consistent approach which enables one to ignore the drop charge is to assume the condition given by (2.2) to be valid for the system. When condition (2.2) holds, and the interface does not bear electric charge, at zero external electric fields the system has the following properties:

(i) the equilibrium electric potential, $\psi_{i,e}$, which is defined with reference to infinity, does not deviate from a zero value

$$\psi_{i,e} = 0; \tag{2.3a}$$

(ii) the equilibrium concentrations of the charge carriers, $c_{i,e}^{(k)}$, within the bulk of each of the liquids are space independent and satisfy the condition set at the interface by (2.1), i.e.

$$\frac{c_i^{(k)}}{c_e^{(k)}} = \alpha; \tag{2.3b}$$

(iii) the concentrations, $c_{i,e}^{(k)}$, satisfy the electroneutrality condition

$$\sum_k Z^{(k)} c_{i,e}^{(k)} = 0. \tag{2.3c}$$

Here, $Z^{(k)}$ is the electric charge of the kth charge carrier expressed in Faraday units.

Within each of the liquids the pressure is uniform and changes sharply at the interface according to the Laplace relationship

$$p_e = 0, \quad p_i = \frac{2\gamma}{a}. \tag{2.4}$$

2.2. *Governing equations and boundary conditions*

The system behaviour after the electric field has been applied will be described using the first-order perturbation technique. Accordingly, we will represent the species concentrations $C_{i,e}^{(k)}$, electric potential, $\Psi_{i,e}$, the local velocity, $\boldsymbol{U}_{i,e}$, and the pressure, $P_{i,e}$ as sums of the relevant equilibrium values, which were discussed in § 2.1, and their variations due to the applied electric field $\delta \boldsymbol{E}$ (respectively, $\delta C_{i,e}^{(k)}$, $\delta \Psi_{i,e}$, $\delta \boldsymbol{U}_{i,e}$, and $\delta P_{i,e}$):

$$C_{i,e}^{(k)} = c_{i,e}^{(k)} + \delta C_{i,e}^{(k)}, \quad \Psi_{i,e} = \psi_{i,e} + \delta \Psi_{i,e} = \delta \Psi_{i,e} \tag{2.5a, b}$$

$$\boldsymbol{U}_{i,e} = \boldsymbol{u}_{i,e} + \delta \boldsymbol{U}_{i,e} = \delta \boldsymbol{U}_{i,e}, \quad P_e = p_e + \delta P_e = \delta P_e, \quad P_i = p_i + \delta P_i = \frac{2\gamma}{a} + \delta P_i. \tag{2.5c, d, e}$$

It should be noted that, in the presence of an electric field, the system shown in figure 1 is characterized by axial symmetry. Since we analyse the behaviour close to the thermodynamic equilibrium, we do not expect any instability (Nicolis & Prigogine 1977) which could break the symmetry. Accordingly, all space distributions are assumed to depend on two coordinates, r and θ, of spherical coordinate system (figure 1). One can introduce the function $r_s(\theta)$, which describes the surface shape of the deformed drop. The spherical shape at $\delta \boldsymbol{E} = 0$ is described by $r_s(\theta) = a$. Using $\delta r_s(\theta)$, we represent $r_s(\theta)$ as

$$r_s(\theta) = a + \delta r_s(\theta). \tag{2.5f}$$

The liquid inside the drop is assumed to be incompressible, and the drop volume variation should be zero. Using (2.5f) one obtains

$$\delta V = 2\pi a^2 \int_0^\pi \delta r_s(\theta) \sin(\theta)\, \mathrm{d}\theta = 0. \tag{2.5g}$$

We will use the interface mean curvature $X(\theta)$ which can be represented as

$$X(\theta) = \frac{1}{a} + \delta X(\theta). \tag{2.5h}$$

The drop deformation given by (1.1) can be expressed as

$$\delta d = \frac{\delta r_s(0) - \delta r_s(\pi/2)}{2a}. \tag{2.6}$$

In this paper, we will evaluate the variation of drop deformation, δd, given by (2.6).

2.2.1. *Balance of normal stresses*

The functions which characterize the deviation of the drop shape from a sphere, $\delta r_s(\theta)$ and δd, are evaluated using a balance of the normal stresses acting on the

interface. In the present theory, the normal stress balance is completely analogous to the relevant equation employed in Taylor's model as well as in the electrokinetic model of Baygents & Saville (1989) and Saville (1997). The force balance at the interface, after making use of (2.5*b–d*, *h*), can be represented in the form

$$\frac{\varepsilon_0}{2}\{\varepsilon_e(\nabla\delta\Psi_e\cdot\boldsymbol{n})^2-\varepsilon_i(\nabla\delta\Psi_i\cdot\boldsymbol{n})^2-(\varepsilon_e-\varepsilon_i)[(\nabla\delta\Psi_i)^2-(\nabla\delta\Psi_i\cdot\boldsymbol{n})^2]\}$$
$$-(\delta P_e-\delta P_i)+\{\eta_e[\nabla\delta\boldsymbol{U}_e+(\nabla\delta\boldsymbol{U}_e)^*]\cdot\boldsymbol{n}-\eta_i[\nabla\delta\boldsymbol{U}_i+(\nabla\delta\boldsymbol{U}_i)^*]\cdot\boldsymbol{n}\}\cdot\boldsymbol{n}=2\gamma\delta X. \tag{2.7}$$

Here, the unit vector $\boldsymbol{n}$ is normal to the interface outward into the external liquid. The superscript $*$ signifies the transpose of the corresponding tensor.

Similarly to the theories of Taylor (1966), Baygents & Saville (1989) and Saville (1997), the first term in (2.7) is the contribution of the Maxwell tensor to the normal stresses. It describes the variation of the normal electric force acting an element at the interface. All other terms on the left-hand side of (2.7) yield variation of the normal mechanical force. The term on the right-hand side of (2.7) yields the variation of the interfacial tension force.

On writing (2.7), it was assumed that $\delta\gamma=0$. This condition is exactly satisfied for the case of zero solute adsorption. In the framework of the Taylor (1966) model, for the case of non-ionic surfactants, the role of this effect was analysed by Vizika & Saville (1992) and Ha & Yang (1995, 1998).

To use equation (2.7), one has to obtain the distributions of the potential ($\delta\Psi_{i,e}$), pressure ($\delta P_{i,e}$) and velocity ($\delta\boldsymbol{U}_{i,e}$) variations. Let us now formulate the boundary problem for obtaining these distributions.

2.2.2. *Distribution of electric potential*

The distribution of the electric field should satisfy the Poisson equation

$$\nabla^2\delta\Psi_{i,e}=-\frac{\delta q_{i,e}}{\varepsilon_{i,e}\varepsilon_0}, \tag{2.8}$$

where $\delta q_{i,e}$, is the volumetric density of the induced *free* charge. It is defined as

$$\delta q_{i,e}=F\sum_k Z^{(k)}\delta C^{(k)}_{i,e}. \tag{2.9}$$

Equation (2.8) contains two unknown functions, $\delta q_{i,e}$ and $\delta\Psi_{i,e}$, and hence an additional equation is required. For equal diffusion coefficients, the continuity equation for the electric current can be also written in term of these two functions only:

$$\nabla\cdot(-\sigma_{i,e}\nabla\delta\Psi_{i,e}-D_{i,e}\nabla\delta q_{i,e})=0, \tag{2.10}$$

where $D_{i,e}$ is the common ionic diffusion coefficient which can differ for the external and internal liquids. In equation (2.10), the vector in brackets is the electric current density: the first and second terms are the migration and diffusion parts, respectively. The convection part is described by the higher-order term, $\delta\boldsymbol{U}_{i,e}\delta q_{i,e}$, which is omitted from (2.10). Using the Einstein relationship between the diffusion coefficient and the migration mobility, it is convenient represent the local conductivity, $\sigma_{i,e}$, as

$$\sigma_{i,e}=D_{i,e}\varepsilon_0\varepsilon_{i,e}\kappa^2_{i,e}. \tag{2.11}$$

In the framework of the first-order perturbation technique, the Debye parameter in (2.11) is expressed through the uniform equilibrium concentrations, $c_{i,e}^{(k)}$, as

$$\kappa_{i,e}^2 = \frac{F^2}{\varepsilon_0 \varepsilon_{i,e} RT} \sum_k (Z^{(k)})^2 c_{i,e}^{(k)}. \tag{2.12}$$

Thus, compared with Taylor's theory, where the electric potential was obtained from a single Laplace equation (1.9), the model presented here involves two equations (2.8) and (2.10) containing two unknown functions, $\delta q_{i,e}$ and $\delta \Psi_{i,e}$.

Equations (2.8) and (2.10) are subject to the following boundary conditions. A uniform electric field strength at infinity is assumed:

$$\nabla \delta \Psi_e = -\delta \boldsymbol{E} \quad \text{at infinity.} \tag{2.13}$$

At the interface, the boundary conditions reflect continuity of the electric potential and of the normal electric current and displacement. These conditions are, respectively, given by

$$\delta \Psi_e = \delta \Psi_i \quad \text{at the interface,} \tag{2.14}$$

$$(\sigma_e \nabla \delta \Psi_e + D_e \nabla \delta q_e - \sigma_i \nabla \delta \Psi_i - D_i \nabla \delta q_i) \cdot \boldsymbol{n} = 0 \quad \text{at the interface,} \tag{2.15}$$

$$(\varepsilon_e \nabla \delta \Psi_e - \varepsilon_i \nabla \delta \Psi_i) \cdot \boldsymbol{n} = 0 \quad \text{at the interface.} \tag{2.16}$$

The last boundary condition is obtained by combining (2.1), (2.5*a*) and (2.9):

$$\frac{\delta q_i}{\delta q_e} = \alpha \quad \text{at the interface.} \tag{2.17}$$

Boundary conditions (2.16) and (2.17) resulted from the fact that the induced charge is attributed to the liquid bulk, not to the interface, as is in Taylor's model. Boundary condition (2.17) is written for the volumetric density of this charge. The condition given by (2.16) was absent in Taylor's theory where the normal electric displacement was discontinuous at the interface.

There is also condition (2.15) which is a modification of Taylor's boundary condition (1.10) for the continuity of the normal electric current density at the interface. The modification amounts to accounting for the additional contribution to the electric current due to the diffusion term, $D_{i,e} \nabla \delta q_{i,e}$. Note that, when $\delta q_{i,e} = 0$, (2.15) is transformed into Taylor's boundary condition (1.10). Simultaneously, the boundary conditions given by (2.16) and (2.17) become redundant since, at $\delta q_{i,e} = 0$, both equations (2.8) and (2.10) are transformed into a single Laplace equation.

It should be noted that, using the simplifying assumptions of the proposed model, the electric part of the problem, which is given by equations (2.8) and (2.10) subject to boundary conditions (2.13)–(2.17), could be obtained from the electrokinetic model presented by Baygents & Saville (1991) and Saville (1997).

2.2.3. *Hydrodynamic stresses*

The mechanical stresses, which are represented in (2.7), are governed by the Navier–Stokes equation set containing the volumetric electric force. Using (2.5*a*, *b*) and (2.9) one can represent the leading terms for volumetric electric force as $-\delta q_{i,e} \nabla \delta \Psi_{i,e}$. In terms of $\delta \boldsymbol{U}_{i,e}$, the inertial forces yield a higher-order contribution than the viscous forces. Hence, the Navier–Stokes equation set can be written as

$$-\eta_{i,e} \nabla \times (\nabla \times \delta \boldsymbol{U}_{i,e}) = \nabla \delta P_{i,e} + \delta q_{i,e} \nabla \delta \Psi_{i,e}, \tag{2.18}$$

$$\nabla \cdot \delta \boldsymbol{U}_{i,e} = 0. \tag{2.19}$$

Equations (2.18) and (2.19) are subject to the following boundary conditions: the external liquid velocity and pressure is zero at infinity

$$\delta \boldsymbol{U}_e = 0 \quad \text{at infinity,} \tag{2.20}$$

$$\delta P_e = 0 \quad \text{at infinity;} \tag{2.21}$$

the normal velocities of both liquids are zero at the interface

$$\delta \boldsymbol{U}_{i,e} \cdot \boldsymbol{n} = 0 \quad \text{at the interface;} \tag{2.22}$$

tangential velocities are continuous at the interface

$$(\delta \boldsymbol{U}_e - \delta \boldsymbol{U}_i) \times \boldsymbol{n} = 0 \quad \text{at the interface;} \tag{2.23}$$

at the interface with no adsorbed solute, the tangential stresses should be continuous

$$\{\eta_e[\nabla \delta \boldsymbol{U}_e + (\nabla \delta \boldsymbol{U}_e)^*] \cdot \boldsymbol{n} - \eta_i[\nabla \delta \boldsymbol{U}_i + (\nabla \delta \boldsymbol{U}_i)^*] \cdot \boldsymbol{n}\} \times \boldsymbol{n} = 0 \quad \text{at the interface.} \tag{2.24}$$

Thus, (2.18)–(2.24) represent the hydrodynamic part of the problem. In contrast to Taylor's model, (2.18) contains the electric volumetric force and (2.24) does not contain the tangential Maxwell stresses.

Strictly speaking (2.7), can be also considered as a boundary condition for equations (2.8), (2.10), (2.18) and (2.19). Thus, solution of these equations subject to boundary conditions (2.7), (2.13)–(2.17) and (2.20)–(2.24) yields the variations of the potential ($\delta \Psi_{i,e}$), the charge density ($\delta q_{i,e}$), the velocity ($\delta \boldsymbol{U}_{i,e}$), the pressure ($\delta P_{i,e}$) and the drop shape ($\delta r_s(\theta)$). The derived variation $\delta r_s(\theta)$ should be substituted into (2.6) to obtain the drop deformation, δd.

2.3. *Final form of the mathematical model*

Without losing accuracy, all the boundary conditions which were set at the deformed interface $r_s(\theta)$ (§ 2.2), can be transferred to the initial spherical interface. For any function $\delta\phi[r_s(\theta)]$ at the interface, one can write

$$\delta\phi[r_s(\theta)] = \delta\phi(a,\theta) + [r_s(\theta) - a]\frac{\partial \delta\phi}{\partial r}(a,\theta) + O[(r_s - a)^2]. \tag{2.25}$$

Since $r_s(\theta) - a = O[(\delta E)^2]$, one can conclude that $\delta\phi[r_s(\theta)] - \delta\phi(a,\theta) = o[(\delta E)^2]$. Applying the boundary conditions at the initial (spherical) interface rather than at the deformed interface gives an error which has the same or even higher order as the terms omitted while deriving (2.7), (2.10), (2.15) and (2.18). Using the Taylor problem, Ajayi (1978) showed that accounting for the interface deformation in the boundary conditions yields corrections of drop deformation of order $(\delta E)^4$.

Due to the opportunity to set the boundary conditions at an *a priori* known spherical interface, equations (2.8) and (2.10) subject to boundary conditions (2.13)–(2.17) form a closed problem formulation. We will use the spherical coordinate system shown in figure 1 and the following normalization:

$$\rho = \frac{r}{a}, \quad \Phi_{i,e} = \frac{\delta \Psi_{i,e}}{a\delta E}, \quad \omega_{i,e} = \frac{\delta q_{i,e}}{\varepsilon_0 \varepsilon_{i,e} \kappa_{i,e}^2 a \delta E}, \quad \tilde{\nabla} = a\nabla = \boldsymbol{i}_\rho \frac{\partial}{\partial \rho} + \frac{\boldsymbol{i}_\theta}{\rho}\frac{\partial}{\partial \theta} \tag{2.26}$$

where $\boldsymbol{i}_\rho$ and $\boldsymbol{i}_\theta$ are unit vectors of the spherical coordinate system in figure 1. Consequently, the equation set given by (2.8) and (2.10) can be rewritten as

$$\tilde{\nabla}^2 \omega_{i,e} = (\kappa_{i,e} a)^2 \omega_{i,e}, \tag{2.27}$$

$$\tilde{\nabla}^2 (\Phi_{i,e} + \omega_{i,e}) = 0. \tag{2.28}$$

Boundary conditions (2.13)–(2.17) are represented, as

$$\Phi_e(\rho,\theta) = -\rho\cos\theta \quad \text{as} \quad \rho \to \infty, \tag{2.29}$$

$$\Phi_e(1,\theta) = \Phi_i(1,\theta), \tag{2.30}$$

$$\frac{\partial \Phi_e}{\partial \rho}(1,\theta) = S\frac{\partial \Phi_i}{\partial \rho}(1,\theta), \tag{2.31}$$

$$\frac{\partial(\Phi_e+\omega_e)}{\partial \rho}(1,\theta) = H\frac{\partial(\Phi_i+\omega_i)}{\partial \rho}(1,\theta), \tag{2.32}$$

$$\omega_i(1,\theta) = \omega_e(1,\theta). \tag{2.33}$$

Equations (2.27) and (2.28) subject to the boundary conditions (2.29)–(2.33) provide distributions of the normalized potential, $\Phi_{i,e}$, and the charge density, $\omega_{i,e}$.

Now we consider the fluid mechanics part of the problem described by (2.18)–(2.24). Introducing the substitutions

$$\Pi_{i,e} = \delta P_{i,e}/\varepsilon_0\varepsilon_e(\kappa_e a)^2(\delta E)^2, \quad \boldsymbol{V}_{i,e} = \delta \boldsymbol{U}_{i,e}\eta_e/\varepsilon_0\varepsilon_e a(\kappa_e a)^2(\delta E)^2, \tag{2.34}$$

we obtain the normalized version of the hydrodynamic equations

$$-\tilde{\nabla}\times(\tilde{\nabla}\times\boldsymbol{V}_e) = \tilde{\nabla}\Pi_e + \omega_e\tilde{\nabla}\Phi_e, \tag{2.35}$$

$$-M\tilde{\nabla}\times(\tilde{\nabla}\times\boldsymbol{V}_i) = \tilde{\nabla}\Pi_i + \alpha\omega_i\tilde{\nabla}\Phi_i, \tag{2.36}$$

$$\tilde{\nabla}\cdot\boldsymbol{V}_{i,e} = 0 \tag{2.37}$$

The boundary condition at infinity is

$$\boldsymbol{V}_e(\rho,\theta) \to 0 \quad \text{as} \quad \rho \to \infty. \tag{2.38}$$

The boundary conditions (2.33)–(2.35) are set at the non-deformed drop surface as

$$V_{i\rho}(1,\theta) = V_{e\rho}(1,\theta) = 0, \tag{2.39}$$

$$V_{i\theta}(1,\theta) = V_{e\theta}(1,\theta), \tag{2.40}$$

$$\frac{\partial(V_{e\theta}/\rho)}{\partial \rho}(1,\theta) = M\frac{\partial(V_{i\theta}/\rho)}{\partial \rho}(1,\theta), \tag{2.41}$$

where $V_{i\rho}$ and $V_{e\rho}$ are the radial components of the internal and external normalized velocity given by (2.34); $V_{i\theta}$ and $V_{e\theta}$ are the relevant tangential components. Making use of the solution obtained for $\Phi_{i,e}(\rho,\theta)$ and $\omega_{i,e}(\rho,\theta)$, equations (2.35)–(2.37) and boundary conditions (2.38)–(2.41) yield the hydrodynamic problem formulation.

Now, we will consider the use of the normal stress balance (2.7). The small variations of the mean curvature, δX, and of the drop shape, $\delta r_s(\theta)$, can be related using a known expression (for example, see Landau & Lifshitz 1987):

$$\delta X = -\frac{1}{a^2}\left\{\delta r_s(\theta) + \frac{1}{2\sin(\theta)}\frac{\mathrm{d}}{\mathrm{d}\theta}\left[\sin(\theta)\frac{\mathrm{d}\delta r_s(\theta)}{\mathrm{d}\theta}\right]\right\}. \tag{2.42}$$

Combining (2.7), (2.26), (2.34) and (2.42) one obtains

$$\frac{S-1}{4}\left\{\left[\frac{\partial \Phi_i}{\partial \theta}(1)\right]^2 + S\left[\frac{\partial \Phi_i}{\partial \rho}(1)\right]^2\right\} - (\kappa_e a)^2\left\{\frac{1}{2}[\Pi_e(1)-\Pi_i(1)]\right.$$
$$\left. - \left[\frac{\partial V_{e\rho}}{\partial \rho}(1) - M\frac{\partial V_{i\rho}}{\partial \rho}(1)\right]\right\} = -\left\{\xi(\theta) + \frac{1}{2\sin(\theta)}\frac{\mathrm{d}}{\mathrm{d}\theta}\left[\sin(\theta)\frac{\mathrm{d}\xi(\theta)}{\mathrm{d}\theta}\right]\right\}. \tag{2.43}$$

The dimensionless function $\xi(\theta)$ is expressed as

$$\xi(\theta) = \delta r_s(\theta)\gamma/\varepsilon_0\varepsilon_e a^2(\delta E)^2. \tag{2.44}$$

Equation (2.43) is subject to a condition which is derived using (2.5g) and (2.44):

$$\int_0^\pi \xi(\theta)\sin(\theta)\,\mathrm{d}\theta = 0. \tag{2.45}$$

Combining (2.6) and (2.44) the drop deformation, δd, can be represented in the form

$$\delta d = \tfrac{1}{2}[\xi(0) - \xi(\pi/2)]\delta W, \tag{2.46}$$

where the dimensionless parameter δW is given by (1.2).

To predict the drop deformation, δd, one should: (i) solve the problem given by (2.27), (2.28) and (2.29)–(2.33); (ii) using the derived functions $\Phi_{i,e}(\rho,\theta)$ and $\omega_{i,e}(\rho,\theta)$, solve the fluid mechanic problem (2.35)–(2.41); (iii) substitute the obtained functions $\Phi_{i,e}(\rho,\theta)$, $\Pi_{i,e}(\rho,\theta)$ and $V_{i,e}(\rho,\theta)$ in (2.43) and solve the resulting equation using (2.45); and finally (iv) substitute the derived function $\xi(\theta)$ into (2.46).

3. Model predictions

3.1. *Distribution of electric charge and potential*

To obtain solution of the axially symmetric boundary problem given by (2.27), (2.28) and (2.29)–(2.33), we expand the unknown functions $\omega_{i,e}(\rho,\theta)$ and $\Phi_{i,e}(\rho,\theta)$ in Legendre polynomials, $p_n[\cos(\theta)]$. Due to the orthogonal property of the Legendre polynomial, only the first Legendre harmonic takes a non-zero value. Accordingly

$$\omega_{i,e}(\rho,\theta) = \omega_{i,e}^{(1)}(\rho)\cos(\theta), \tag{3.1}$$

$$\Phi_{i,e}(\rho,\theta) = \Phi_{i,e}^{(1)}(\rho)\cos(\theta). \tag{3.2}$$

The first Legendre harmonics $\omega_{i,e}^{(1)}(\rho)$ and $\Phi_{i,e}^{(1)}(\rho)$ satisfy

$$\frac{\mathrm{d}^2\omega_{i,e}^{(1)}}{\mathrm{d}\rho^2} + \frac{2}{\rho}\frac{\mathrm{d}\omega_{i,e}^{(1)}}{\mathrm{d}\rho} - \left[\frac{2}{\rho^2} + (\kappa a)^2\right]\omega_{i,e}^{(1)} = 0, \tag{3.3}$$

$$\frac{\mathrm{d}^2(\Phi_{i,e}^{(1)} + \omega_{i,e}^{(1)})}{\mathrm{d}\rho^2} + \frac{2}{\rho}\frac{\mathrm{d}(\Phi_{i,e}^{(1)} + \omega_{i,e}^{(1)})}{\mathrm{d}\tilde{r}} - \frac{2(\Phi_{i,e}^{(1)} + \omega_{i,e}^{(1)})}{\rho^2} = 0, \tag{3.4}$$

which are subject to the boundary conditions

$$\Phi_e^{(1)} = -\rho \quad \text{as} \quad \rho \to \infty, \tag{3.5}$$

$$\omega_e^{(1)} = 0 \quad \text{as} \quad \rho \to \infty, \tag{3.6}$$

$$\Phi_e^{(1)}(1) = \Phi_i^{(1)}(1), \tag{3.7}$$

$$\frac{\mathrm{d}\Phi_e^{(1)}}{\mathrm{d}\rho}(1) = S\frac{\mathrm{d}\Phi_i^{(1)}}{\mathrm{d}\rho}(1), \tag{3.8}$$

$$\frac{\mathrm{d}(\Phi_e^{(1)} + \omega_e^{(1)})}{\mathrm{d}\rho}(1) = H\frac{\mathrm{d}(\Phi_i^{(1)} + \omega_i^{(1)})}{\mathrm{d}\rho}(1), \tag{3.9}$$

$$\omega_e^{(1)}(1) = \omega_i^{(1)}(1). \tag{3.10}$$

Solution of the problem given by (3.3)–(3.10) yields $\omega_{i,e}^{(1)}(\rho)$ and $\Phi_{i,e}^{(1)}(\rho)$:

$$\omega_e^{(1)}(\rho) = G\frac{\kappa_e a\rho + 1}{\kappa_e a + 1}\frac{\exp[-\kappa_e a(\rho - 1)]}{\rho^2}, \tag{3.11}$$

$$\omega_i^{(1)}(\rho) = \frac{G}{\rho^2}\frac{\kappa_i a\rho\cosh(\kappa_i a\rho) - \sinh(\kappa_i a\rho)}{\kappa_i a\cosh(\kappa_i a) - \sinh(\kappa_i a)}, \tag{3.12}$$

$$\Phi_e^{(1)}(\rho) = -\rho + \frac{1}{\rho^2}\frac{H-1}{H+2} - \frac{G}{\rho^2}\frac{\kappa_e a\rho + 1}{\kappa_e a + 1}\exp[-\kappa_e a(\rho - 1)], \tag{3.13}$$

$$\Phi_i^{(1)}(\rho) = -\frac{3}{H+2}\rho - \frac{G}{\rho^2}\frac{\kappa_i a\rho\cosh(\kappa_i a\rho) - \sinh(\kappa_i a\rho)}{\kappa_i a\cosh(\kappa_i a) - \sinh(\kappa_i a)}. \tag{3.14}$$

Here, G is a constant given by

$$G = 3\frac{S-H}{H+2}\frac{1}{2(S-1) - \dfrac{S(\kappa_i a)^2}{\kappa_i a\coth(\kappa_i a) - 1} - \dfrac{(\kappa_e a)^2}{\kappa_e a + 1}}. \tag{3.15}$$

Thus, equations (3.1), (3.2) and (3.11)–(3.15) yield space distributions of the normalized charge density and electric potential outside and inside the drop.

3.2. *Prediction of the mechanical stresses*

Continuity equation (2.37) gives the following representation of the normalized local velocity, $\boldsymbol{V}_{i,e}$, inside and outside the drop:

$$\boldsymbol{V}_{i,e} = -\frac{\boldsymbol{i}_\rho}{\rho^2\sin\theta}\frac{\partial\Omega_{i,e}}{\partial\theta} + \frac{\boldsymbol{i}_\theta}{\rho\sin\theta}\frac{\partial\Omega_{i,e}}{\partial\rho}. \tag{3.16}$$

Here, $\Omega_{i,e}(\rho,\theta)$ is the Stokes stream function of the internal and external liquids, respectively. Applying the operator $\nabla\times$ to both sides of each of (2.35) and (2.36) and making use of the substitution given by (3.16), we obtain a scalar equation for $\Omega_{i,e}(\rho,\theta)$. Expression (3.16) is also substituted into boundary conditions (2.38)–(2.41). Then, we expand $\Omega_{i,e}(\rho,\theta)$ in the Gegenbauer polynomial series. Due to the orthogonal property of the Gegenbauer polynomials, only the third Gegenbauer harmonic takes a non-zero value. Accordingly

$$\Omega_{i,e}(\rho,\theta) = \Omega_{i,e}^{(3)}(\rho)\cos(\theta)\sin^2(\theta). \tag{3.17}$$

Here, the function $\Omega_{i,e}^{(3)}(\rho)$ is obtained as a solution of equations

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} - \frac{6}{\rho^2}\right)^2\Omega_e^{(3)}(\rho) = -G\frac{3\rho(\kappa_e a\rho + 1) + (\kappa_e a)^2\left(\rho^3 - \dfrac{H-1}{H+2}\right)}{\kappa_e a + 1}\frac{\exp[-\kappa_e a(\rho-1)]}{\rho^3}, \tag{3.18}$$

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} - \frac{6}{\rho^2}\right)^2\Omega_i^{(3)}(\rho) = -\frac{9\alpha G}{M(H+2)\rho^2}\frac{\kappa_i a\cosh(\kappa_i a\rho) - [1 + (\kappa_i a\rho)^2/3]\sinh(\kappa_i a\rho)}{\kappa_i a\cosh(\kappa_i a) - \sinh(\kappa_i a)} \tag{3.19}$$

subject to the following boundary conditions

$$\frac{\Omega_e^{(3)}}{\rho^2} \to 0 \quad \text{as} \quad \rho\to\infty, \tag{3.20}$$

$$\Omega_i^{(3)}(1) = \Omega_e^{(3)}(1) = 0, \tag{3.21}$$

$$\frac{\mathrm{d}\Omega_i^{(3)}}{\mathrm{d}\rho}(1) = \frac{\mathrm{d}\Omega_e^{(3)}}{\mathrm{d}\rho}(1), \tag{3.22}$$

$$\frac{\mathrm{d}^2\Omega_e^{(3)}}{\mathrm{d}\rho^2}(1) - 2\frac{\mathrm{d}\Omega_e^{(3)}}{\mathrm{d}\rho}(1) = M\left[\frac{\mathrm{d}^2\Omega_i^{(3)}}{\mathrm{d}\rho^2}(1) - 2\frac{\mathrm{d}\Omega_i^{(3)}}{\mathrm{d}\rho}\right]. \tag{3.23}$$

Solution of the problem given by (3.18)–(3.23) takes the form

$$\begin{aligned}\Omega_e^{(3)}(\rho) = {} & \frac{5(\rho^2-1)}{2\rho^2}Q + \frac{G}{1680(\kappa_e a+1)}\left\{\left[\left((\kappa_e a)^5\rho^4 - (\kappa_e a)^4\rho^3\right.\right.\right. \\ & -26(\kappa_e a)^3\rho^2 + 22(\kappa_e a)^2\rho - 32\kappa_e a + \frac{48}{\rho} + \frac{48}{\kappa_e a\rho^2}\Bigg)\frac{H-1}{H+2} \\ & \left.\left.\left. -\frac{1680}{(\kappa_e a)^2}\left(\frac{3}{(\kappa_e a)^2\rho} + \frac{3}{\kappa_e a\rho} + 1\right)\right]\exp[-\kappa_e a(\rho-1)] - \frac{(\kappa_e a)^4\exp(\kappa_e a)}{2}\frac{H-1}{H+2}\right. \\ & \times\left[\left(\frac{5(\kappa_e a)^2-84}{\rho^2} + 7(20-(\kappa_e a)^2)\right)E_1(\kappa_e a) + 2\rho^3((\kappa_e a)^2\rho^2 - 28)E_1(\kappa_e a\rho)\right] \\ & -\frac{7\kappa_e a}{2}\frac{H-1}{H+2}[(\kappa_e a)^4 - (\kappa_e a)^3 - 18(\kappa_e a)^2 + 14\kappa_e a - 16] - \frac{840(\kappa_e a+1)}{(\kappa_e a)^2} \\ & -\frac{1}{2(\kappa_e a)^4\rho^2}\left[(-5(\kappa_e a)^6 + 5(\kappa_e a)^5 + 74(\kappa_e a)^4 - 54(\kappa_e a)^3 + 48(\kappa_e a)^2 + 96\kappa_e a + 96)\right. \\ & \left.\left.\times(\kappa_e a)^3\frac{H-1}{H+2} - 1680(\kappa_e a)^2(\kappa_e a+3) - 10080(\kappa_e a+1)\right]\right\}\end{aligned} \tag{3.24}$$

and

$$\begin{aligned}\Omega_i^{(3)}(\rho) = {} & \frac{5}{2}Q\rho^3(\rho^2-1) + \frac{3\alpha G}{(H+2)M(\kappa_i a)^3[\kappa_i a\cosh(\kappa_i a) - \sinh(\kappa_i a)]} \\ & \times\left\{\frac{3+(\kappa_i a)^2\rho^2}{\kappa_i a\rho^2}\sinh(\kappa_i a\rho) - \frac{3\cosh(\kappa_i a\rho)}{\rho}\right. \\ & +\rho^3\left[\frac{3(5+2(\kappa_i a)^2)\rho^2 - 21 - 8(\kappa_i a)^2}{2\kappa_i a}\sinh(\kappa_i a)\right. \\ & \left.\left.-\frac{(15+(\kappa_i a)^2)\rho^2 - 21 - (\kappa_i a)^2}{2}\cosh(\kappa_i a)\right]\right\}.\end{aligned} \tag{3.25}$$

Here, the constant Q is given by

$$\begin{aligned}Q = {} & -\frac{G}{25(1+M)(\kappa_e a+1)}\left\{1 + 3\alpha\frac{\kappa_e a+1}{(\kappa_i a)^4[\kappa_i a\coth(\kappa_i a) - 1]}\right. \\ & \times\frac{[(\kappa_i a)^4 + 45(\kappa_i a)^2 + 105] - 5\kappa_i a[(\kappa_i a)^2 + 21]\coth(\kappa_i a)}{H+2} \\ & \left.+(\kappa_e a)^2\frac{H-1}{H+2}\frac{(\kappa_e a)^2[(\kappa_e a)^2 - 12]\exp(\kappa_e a)E_1(\kappa_e a) - (\kappa_e a+3)[(\kappa_e a)^2 - 4\kappa_e a + 2]}{48}\right\}.\end{aligned} \tag{3.26}$$

The function $E_1(\kappa_e a)$ employed in (3.24)–(3.26) is the exponential integral given by

$$E_1(\kappa_e a) = \int_{\kappa_e a}^{\infty} \frac{\exp(-t)}{t}\,\mathrm{d}t. \tag{3.27}$$

To obtain the pressure, we substitute (3.1), (3.2), (3.16) and (3.17) into (2.35) and (2.36). After some transformations, we obtain expressions for the complete differential:

$$\mathrm{d}\Pi_e = -\left[\frac{1}{\rho^2\sin(\theta)}\frac{\partial(L^2\Omega_e)}{\partial\theta} + \omega_e\frac{\partial\Phi_e}{\partial\rho}\right]\mathrm{d}\rho + \left[\frac{1}{\sin(\theta)}\frac{\partial(L^2\Omega_e)}{\partial\rho} - \omega_e\frac{\partial\Phi_e}{\partial\theta}\right]\mathrm{d}\theta, \tag{3.28}$$

$$\mathrm{d}\Pi_i = -\left[\frac{1}{\rho^2\sin(\theta)}\frac{\partial(L^2\Omega_i)}{\partial\theta} + \alpha\omega_i\frac{\partial\Phi_i}{\partial\rho}\right]\mathrm{d}\rho + \left[\frac{M}{\sin(\theta)}\frac{\partial(L^2\Omega_i)}{\partial\rho} - \alpha\omega_i\frac{\partial\Phi_i}{\partial\theta}\right]\mathrm{d}\theta. \tag{3.29}$$

Combining (3.1), (3.2), (3.28) and (3.29) and integrating the expression obtained yields

$$\Pi_e(\rho,\theta) = \frac{1-3\cos^2\theta}{6}\left[\frac{\mathrm{d}}{\mathrm{d}\rho}\left(\frac{\mathrm{d}^2\Omega_e^{(3)}}{\mathrm{d}\rho^2} - 6\frac{\Omega_e^{(3)}}{\rho^2}\right) + \Phi_e^{(1)}\omega_e^{(1)}\right] + \frac{1}{3}\int_{\rho}^{\infty}\left[\frac{\mathrm{d}\Phi_e^{(1)}}{\mathrm{d}x}\omega_e^{(1)}\right]\mathrm{d}x, \tag{3.30}$$

$$\Pi_i(\rho,\theta) = \Pi_i(0) + \frac{1-3\cos^2\theta}{6}\left[M\frac{\mathrm{d}}{\mathrm{d}\rho}\left(\frac{\mathrm{d}^2\Omega_i^{(3)}}{\mathrm{d}\rho^2} - 6\frac{\Omega_i^{(3)}}{\rho^2}\right) + \alpha\Phi_i^{(1)}\omega_i^{(1)}\right] - \frac{\alpha}{3}\int_0^{\rho}\left[\frac{\mathrm{d}\Phi_i^{(1)}}{\mathrm{d}x}\omega_i^{(1)}\right]\mathrm{d}x, \tag{3.31}$$

where $\Pi_i(0)$ is the normalized pressure in the centre of the drop.

The normalized radial velocity, which is present in (2.55), is obtained by combining (3.16) and (3.17):

$$V_{i,e\rho} = \frac{\Omega_{i,e}^{(3)}}{\rho^2}(1-3\cos^2\theta). \tag{3.32}$$

Expressions (3.30)–(3.32) combined with (3.14)–(3.16) and (3.33)–(3.35) yield functions which are employed in (2.43).

3.3. *Prediction of the drop deformation*

According to (2.46), to predict the drop deformation, δd, one has to determine the function $\xi(\theta)$ from (2.43). To this end, we combine (3.1), (3.2), (3.17), (3.30)–(3.32) and (2.43), and represent $\xi(\theta)$ using a series of the Legendre polynomials, $p_n[\cos(\theta)]$. Due to condition (2.45) and to the orthogonal properties of the Legendre polynomials, only the second Legendre harmonic, $\xi^{(2)}$, takes a non-zero value. Consequently, expression (2.46) for the drop deformation, δd, is rewritten as

$$\delta d = \tfrac{3}{4}\xi^{(2)}\delta W, \tag{3.33}$$

where $\xi^{(2)}$ takes the form

$$\xi^{(2)} = \frac{S-1}{12}\left\{S\left[\frac{\partial\Phi_i^{(1)}}{\partial\rho}(1)\right]^2 - [\Phi_i^{(1)}(1)]^2\right\} + \frac{(\kappa_e a)^2}{12}\left[\frac{\mathrm{d}^3\Omega_e^{(3)}}{\mathrm{d}\rho^3}(1) - M\frac{\mathrm{d}^3\Omega_i^{(3)}}{\mathrm{d}\rho^3}(1) - 18(1-M)\frac{\mathrm{d}\Omega_i^{(3)}}{\mathrm{d}\rho}(1) - (\alpha-1)\Phi_i^{(1)}(1)\omega_i^{(1)}(1)\right]. \tag{3.34}$$

Using (3.11)–(3.15) and (3.24) (3.26) to obtain the functions represented in (3.34), we derive the final expression for the drop deformation:

$$\frac{\delta d}{\delta W} = \frac{9}{16(H+2)^2} \times \left[(S-1)^2 + \frac{S-H}{2(S-1)-(\kappa_e a)^2/(\kappa_e a+1)-S\psi(\kappa_i a)} \Lambda(H,S,M,\kappa_e a,\kappa_i a)\right], \tag{3.35}$$

where the function $\Lambda(H,S,M,\kappa_e a,\kappa_i a)$ is given by

$$\begin{aligned}\Lambda = {} & S\left\{\frac{5-M}{1+M} - 4S + \frac{21(3+2M)}{(1+M)(\kappa_i a)^2}[3-\psi(\kappa_i a)] + \psi(\kappa_i a)\left(\frac{3}{5}\frac{2+3M}{1+M} + 2S\right)\right\} \\ & + \frac{(\kappa_e a)^6(H-1)}{240}\frac{(2+3M)(\kappa_e a)^2 - 4(16+19M)}{(1+M)(\kappa_e a+1)}\exp(\kappa_e a)E_1(\kappa_e a) \\ & + \frac{(\kappa_e a)^4(H-1)}{240(\kappa_e a+1)}\left\{40(\kappa_e a-1) - (\kappa_e a+3)[(\kappa_e a)^2 - 4\kappa_e a + 2]\frac{2+3M}{M+1}\right\} \\ & + \frac{(\kappa_e a)^2(H+2)}{5(\kappa_e a+1)}\left[\frac{2+3M}{M+1} + \frac{5}{3}(3+\kappa_e a)\right] + 2 - (\kappa_e a)^2 \\ & + (S-H)\frac{(S-1)\{S[2-\psi(\kappa_i a)]^2 - 1\} + (\kappa_i a)^2 S - (\kappa_e a)^2}{2(S-1)-(\kappa_e a)^2/(\kappa_e a+1)-S\psi(\kappa_i a)},\end{aligned} \tag{3.36}$$

where we introduced the notation

$$\psi(\kappa_i a) = \frac{(\kappa_i a)^2}{\kappa_i a \coth(\kappa_i a) - 1}. \tag{3.37}$$

Equations (3.35)–(3.37) represent the normalized drop deformation, $\delta d/\delta W$, as an explicit function of the parameters H, S and M, which were employed in the previous theory of Taylor (1966), together with two additional parameters $\kappa_i a$ and $\kappa_e a$ which are specific to the present theory.

4. Analysis of limiting cases

Now, we will discuss the limiting cases, when the additional parameters, $\kappa_i a$ and $\kappa_e a$ approach either zero or infinity. First, we will show that, for these limiting cases, the result of the present model is transformed into expressions obtained earlier by others.

4.1. *Perfect dielectric in perfect dielectric (OTAM limit)*

Taking into account (2.12) and assuming that $c_{i,e}^{(k)} \to 0$ one can conclude that for perfect dielectrics

$$\kappa_e a \to 0, \quad \kappa_i a \to 0. \tag{4.1}$$

For $\kappa_i a \ll 1$, the function $\psi(\kappa_i a)$ given by (3.37) takes following asymptotic form:

$$\psi(\kappa_i a) = 3 + \frac{(\kappa_i a)^2}{5} + O((\kappa_i a)^4). \tag{4.2}$$

Combining (3.35), (3.36) and (4.2), making use of the limiting transition given by (4.1) and retaining only leading terms, one obtains

$$\lim_{\substack{\kappa_e a\to 0\\ \kappa_i a\to 0}}\left(\frac{\delta d}{\delta W}\right)=\frac{9}{16(H+2)^2}\left\{(S-1)^2+\frac{S-H}{2(S-1)-3S}\right.$$
$$\times\left[S\left[\frac{5-M}{1+M}-4S-\frac{21(3+2M)}{5(1+M)}+3\left(\frac{3}{5}\frac{2+3M}{1+M}+2S\right)\right]+2\right.$$
$$\left.\left.+\frac{(S-H)[(S-1)[S(2-3)^2-1]]}{2(S-1)-3S}\right]\right\}=\frac{9(S-1)^2}{16(S+2)^2}. \tag{4.3}$$

As it would be expected, (4.3) coincides with the OTAM result (1.3).

4.2. *Taylor's limit*

The present electrokinetic model should yield the same result as the leaky dielectric model provided that the thickness of the space charge regions approaches zero. This limiting case corresponds to the limiting transition given by $\kappa_e a\to\infty$ and $\kappa_i a\to\infty$. Accordingly, one might expect the result given by (3.35)–(3.37) to be transformed into Taylor's expression (1.4) only if the conditions $\kappa_e a\to\infty$ and $\kappa_i a\to\infty$ are simultaneously satisfied. However, surprisingly, the result (3.35)–(3.37) approaches (1.4) when only one of the parameters $\kappa_e a$ and $\kappa_i a$ approaches infinity. The other parameter can take an arbitrary value.

Let us now consider the limiting transition of (3.35)–(3.37) when $\kappa_e a\to\infty$ and $\kappa_i a$ is arbitrary. For $\kappa_e a\gg 1$, expressions (3.35)–(3.37) are reduced to

$$\frac{\delta d}{\delta W}=\frac{9}{16(H+2)^2}\left\{(S-1)^2+(H-S)\right.$$
$$\times\left[\frac{(\kappa_e a)^5(H-1)}{240}\frac{(2+3M)(\kappa_e a)^2-4(16+19M)}{(1+M)(\kappa_e a+1)}\exp(\kappa_e a)E_1(\kappa_e a)\right.$$
$$+\frac{(\kappa_e a)^3(H-1)}{240(\kappa_e a+1)}\left\{40(\kappa_e a-1)-(\kappa_e a+3)[(\kappa_e a)^2-4\kappa_e a+2]\frac{2+3M}{M+1}\right\}$$
$$\left.\left.+\frac{\kappa_e a}{5(\kappa_e a+1)}\left[\frac{2+3M}{M+1}+\frac{5}{3}(3+\kappa_e a)\right]-\kappa_e a\right]\right\}+O(1/\kappa_e a). \tag{4.4}$$

To obtain the correct asymptotic form of the final result one must retain at least six leading terms in the expansion of $E_1(\kappa_e a)$ for $\kappa_e a>1$:

$$E_1(\kappa_e a)=\frac{\exp(-\kappa_e a)}{\kappa_e a}\left\{1-\frac{1}{\kappa_e a}+\frac{2}{(\kappa_e a)^2}-\frac{6}{(\kappa_e a)^3}+\frac{24}{(\kappa_e a)^4}\right.$$
$$\left.-\frac{120}{(\kappa_e a)^5}+O\left[\frac{1}{(\kappa_e a)^6}\right]\right\}. \tag{4.5}$$

Combining (4.4) and (4.5) we obtain

$$\frac{\delta d}{\delta W}=\frac{9}{16(H+2)^2}\left[H^2+1-2S+\frac{3}{5}(H-S)\frac{2+3M}{1+M}\right]+O(1/\kappa_e a). \tag{4.6}$$

Thus, as $\kappa_e a\to\infty$, the drop deformation approaches Taylor's value given by (1.4).

When $\kappa_i a\to\infty$, the function $\psi(\kappa_i a)$ given by (3.37) is approximated as

$$\psi(\kappa_i a)=\kappa_i a[1+O(1/\kappa_i a)]. \tag{4.7}$$

Using (4.7) and combining (3.35)–(3.37) one can show that

$$\frac{\delta d}{\delta W} = \frac{9}{16(H+2)^2}\left\{(S-1)^2 + \frac{H-S}{S\kappa_i a}\left[S\kappa_i a\left(\frac{3}{5}\frac{2+3M}{1+M}+2S\right)\right.\right.$$
$$\left.\left.+(H-S)S\kappa_i a\right]\right\} + O(1/\kappa_i a)$$
$$= \frac{9}{16(H+2)^2}\left[1+H^2-2S+\frac{3}{5}(H-S)\frac{2+3M}{1+M}\right] + O(1/\kappa_i a). \qquad (4.8)$$

Hence, at the limit $\kappa_i a \to \infty$, equations (3.35)–(3.37) yield Taylor's expression (1.4), as well. Thus, to obtain Taylor's result (1.4), it is sufficient to consider the limiting transition of (3.35)–(3.37) either as $\kappa_e a \to \infty$ or as $\kappa_i a \to \infty$ and not requiring the simultaneous infinite increase of the two parameters.

To explain the behaviour of the limits discussed above, we combine (2.12), (2.26), (3.1), (3.2), (3.11) and (3.12) to represent the internal and external electric charge densities at the interface, $\delta q_{i,e}(a)$, as

$$\delta q_{i,e}(a) = 3\frac{S-H}{H+2}\frac{\varepsilon_0\varepsilon_{i,e}\kappa_{i,e}^2 a\delta E}{2(S-1)-S(\kappa_i a)^2/(\kappa_i a\coth(\kappa_i a)-1)-(\kappa_e a)^2/(\kappa_e a+1)}\cos(\theta). \qquad (4.9)$$

It is noted from (4.9) that $\delta q_i(a) \to 0$ as $\kappa_e a \to \infty$, and $\delta q_e(a) \to 0$ as $\kappa_i a \to \infty$. Hence, when either the internal or external electric charge layer becomes infinitely thin, the charge of the other layer (having non-zero thickness) approaches zero. Accordingly, all the induced free charge is concentrated within the infinitely thin layer and the system becomes the same as that described by the model of Taylor.

4.3. *Conducting drop in perfect dielectric*

Now we will consider the case of a conducting drop surrounded by a perfect dielectric. It corresponds to the limiting case

$$\kappa_e a \to 0. \qquad (4.10)$$

Using relation (2.11) one obtains

$$H = S(\kappa_i a/\kappa_e a)^2\frac{D_e}{D_i}. \qquad (4.11)$$

Due to the relationship (4.11), for given S and D_e/D_i condition (4.10) yields

$$H \to \infty. \qquad (4.12)$$

At the simultaneous limits given by (4.10) and (4.12), equations (3.35)–(3.37) reduce to

$$\frac{\delta d}{\delta W} = \frac{9}{16}\frac{(S-1)\{S[2-(\kappa_i a)^2/(\kappa_i a\coth(\kappa_i a)-1)]^2-1\}+(\kappa_i a)^2 S}{[2(S-1)-S(\kappa_i a)^2/(\kappa_i a\coth(\kappa_i a)-1)]^2}. \qquad (4.13)$$

Equation (4.13) describes the behaviour of the drop deformation for the case of a conducting drop surrounded by a perfect dielectric medium.

As $\kappa_i a \to 0$, one obtains from (4.1) the OTAM limiting case given by (1.3). As $\kappa_i a \to \infty$, the limiting transition in (4.13) yields (1.5) which is the common limit of the OTAM (at $S \to \infty$) and Taylor (at $H \to \infty$) theories. There is also another expected

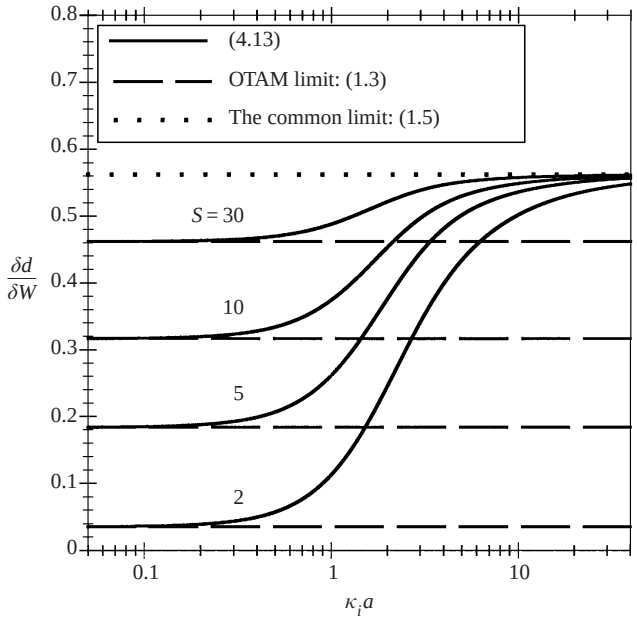

FIGURE 2. A conducting drop in a perfect dielectric liquid. Variation of the normalized drop deformation, $\delta d/\delta W$, with $\kappa_i a$, for different values of $S = \varepsilon_i/\varepsilon_e$.

limiting transition which enables (1.5) to be obtained from (4.13). When $S \to \infty$, the terms depending on $\kappa_i a$ are cancelled out and (4.13) is transformed into (1.5) as well.

Note that the right-hand side of (4.13) does not contain parameter M. Such a situation occurs because, under the conditions given by (4.10) and (4.12), no hydrodynamic flow occurs inside and outside the drop. It is also remarkable that no local electric current and no individual species transfer occur in the system under consideration. As $\kappa_e a \to 0$ and $H \to \infty$, all charge distributions present in the system are of equilibrium nature.

The variation of the normalized drop deformation, $\delta d/\delta W$, with $\kappa_i a$ is given in figure 2. The solid curves, which plot (4.13) for different S, display an increase in prolate deformation with $\kappa_i a$. At sufficiently small $\kappa_i a$, each of the solid curves approaches the corresponding limit given by (1.3). For larger $\kappa_i a$, the curves for all S values approach the limiting case of $\delta d/\delta W = 9/16$ as given by (1.5).

4.4. *Perfect dielectric drop in conducting liquid*

This situation corresponds to the limit

$$\kappa_i a \to 0. \tag{4.14}$$

Using (4.11), for given values of S and D_i/D_e one obtains from (4.14) the limit of

$$H \to 0. \tag{4.15}$$

At the limits defined by (4.14) and (4.15), using asymptotic expression (4.2), the result given by (3.35)–(3.37) is transformed to

$$\frac{\delta d}{\delta W} = \frac{9}{64}\left[(S-1)^2 - \frac{S}{S+2+(\kappa_e a)^2/(\kappa_e a+1)}\Lambda(S,M,\kappa_e a)\right] + O\left(\frac{1}{\kappa_i a}\right) \tag{4.16}$$

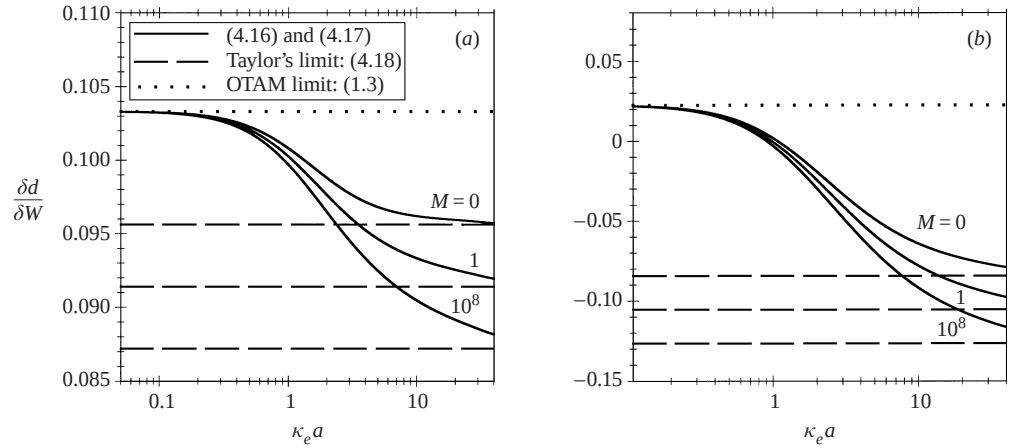

FIGURE 3. A perfect dielectric drop in a conducting liquid. Variation of normalized drop deformation, $\delta d/\delta W$, with $\kappa_e a$ for different values of $M = \eta_i/\eta_e$: (*a*) $S = \varepsilon_i/\varepsilon_e = 0.1$; (*b*) $S = \varepsilon_i/\varepsilon_e = 0.5$.

A simplified form of the function $\Lambda(S, M, \kappa_e a)$ is

$$\Lambda = 2S(S-2) - \frac{(\kappa_e a)^6}{240}\frac{(2+3M)(\kappa_e a)^2 - 4(16+19M)}{(1+M)(\kappa_e a+1)}\exp(\kappa_e a)E_1(\kappa_e a)$$
$$-\frac{(\kappa_e a)^4}{240(\kappa_e a+1)}\left\{40(\kappa_e a-1) - (\kappa_e a+3)[(\kappa_e a)^2 - 4\kappa_e a + 2]\frac{2+3M}{M+1}\right\}$$
$$+\frac{2(\kappa_e a)^2}{5(\kappa_e a+1)}\left[\frac{2+3M}{M+1} + \frac{5}{3}(3+\kappa_e a)\right] + 2 - (\kappa_e a)^2$$
$$-\frac{S[(S-1)^2 - (\kappa_e a)^2]}{S+2+(\kappa_e a)^2/(\kappa_e a+1)}. \tag{4.17}$$

Equations (4.16) and (4.17) describe the deformation of a perfect dielectric drop in a conducting liquid.

As was expected, for $\kappa_e a \to 0$ (4.16) and (4.17) yield the result given by (1.3). As $\kappa_e a \to \infty$, using (4.5), one obtains from (4.16) and (4.17) the following limiting expression:

$$\frac{\delta d}{\delta W} = \frac{9}{64}\left(1 - 2S - \frac{3}{5}S\frac{2+3M}{1+M}\right). \tag{4.18}$$

Expression (4.18) coincides with the limit of (1.4) at $H \to 0$. When $S \to 0$, the result given by (4.16) and (4.17) does not depend on $\kappa_e a$. The right-hand side of (4.18) takes the value $9/64$ that corresponds to the limit of Taylor's expression (1.4) as $H \to 0$ and $S \to 0$.

Variation of the normalized drop deformation, $\delta d/\delta W$, with $\kappa_e a$ is illustrated by the curves given in figures 3(*a*) and 3(*b*). The solid curves, which were plotted according to (4.16) and (4.17) for different M, display a decrease in $\delta d/\delta W$ with increasing $\kappa_e a$. For sufficiently small $\kappa_e a$, the curves plotted for different M coincide with the OTAM result, (1.3). With increasing $\kappa_e a$, each of the curves approaches a corresponding asymptote defined by (4.18). The negative values of $\delta d/\delta W$ in figure 3(*b*) correspond to an oblate shape. This behaviour will be discussed next.

5. Discussion

The applicability of the main result given by (3.35)–(3.37) is limited by the assumptions of equal diffusion coefficients and zero liquid drop charge. Therefore, when, for example, KCl ions dominate in the liquids, and the drops bear sufficiently low electric charge, one can expect a quantitative agreement between the present theory and the experiment. At the same time, for $H \gg 10$, one can use the model of a conducting drop in a perfect dielectric liquid. The relevant limiting case is described by equation (4.13) (§ 4.3). Although (4.13) was obtained for equal diffusion and distribution coefficients, it is valid for any ionic system. This is because of the thermodynamic equilibrium, which holds even under the influence of external electric field in the case of zero ionic concentrations in the outer liquid. The result from thermodynamic considerations should exactly coincide with (4.13) which does not contain either diffusion coefficients or other irreversible process parameters, H and M.

Within the framework of the limiting assumptions, the present theory is 'chemically independent', i.e. it is valid for an arbitrary ionic system regardless of the chemical reactions between the species. Such a property exists only for the case of equal diffusion and distribution coefficients. For this case only, one can use a single continuity equation (2.10), for the electric current, instead of set of continuity equations for each carrier flux, Saville (1997).

Being 'chemically independent', the present theory is like Taylor's theory where the origin of the charge carriers is not specified. However, Taylor's model is independent of the ionic system even for the case of large drop deformations (Sherwood 1988; Feng 1999). Alternatively, using the present model for large drop deformations, one always needs to specify the ionic system and the chemical reaction between the species. This becomes clear from the structure of equation (2.10). Adding the convection term, $\delta \boldsymbol{U}_{i,e} \delta q_{i,e}$ inside the brackets in (2.10), one can use this equation to describe large deformations. However, for this case, one should consider the conductivity $\sigma_{i,e}$ to be function of the unknown concentrations $C_{i,e}^{(k)} = c_{i,e}^{(k)} + \delta C_{i,e}^{(k)}$. Due to the presence of the additional unknown functions, $\delta C_{i,e}^{(k)}$, equation set (2.8) and (2.11) should be completed by the continuity equations for the individual species fluxes, Saville (1997).

It should be also noted that, when considering large drop deformations, one can ignore inertial terms in (2.18), for low Reynolds numbers only.

The main result of the present paper, (3.35)–(3.37), represents the normalized drop deformation, $\delta d/\delta W$, as a function of all the parameters, H, S and M, employed in the previous theories (O'Konski & Thacher 1953; Allan & Mason 1962; Taylor 1966), as well as the additional parameters $\kappa_i a$ and $\kappa_e a$. The latter parameters can be related using either (4.11) or

$$\frac{\kappa_i a}{\kappa_e a} = \left(\frac{\alpha}{S}\right)^{1/2}. \tag{5.1}$$

Equation (5.1) is obtained by combining (2.3*b*) and (2.12). Using (4.11) or (5.1), one of the additional parameters, $\kappa_i a$ or $\kappa_e a$, can be expressed through the other one. Consequently, the main result will depend on H, S and M, $\kappa_i a$ (or $\kappa_e a$), and on one of the new parameters, either α or D_i/D_e.

The number of parameters can be reduced using the Einstein–Stokes relation for the diffusion coefficients. Assuming equal ionic radii in both liquids, the Einstein–Stokes relation yields

$$\frac{D_e}{D_i} = M. \tag{5.2}$$

Combining (4.11) with (5.2) enables one to express $\kappa_i a$ through $\kappa_e a$ (or vice versa) and the parameters H, S and M:

$$\frac{\kappa_i a}{\kappa_e a} = \left(\frac{H}{S} M\right)^{1/2}. \tag{5.3}$$

Thus, simultaneously using (3.35)–(3.37) and (5.3), the normalized drop deformation, $\delta d/\delta W$, is expressed through Taylor's parameters, H, S and M, together with only one additional parameter, either $\kappa_i a$ or $\kappa_e a$.

According to the results of the previous theories (O'Konski & Thacher 1953; Allan & Mason 1962; Taylor 1966) the normalized drop deformations, $\delta d/\delta W$, is independent of the drop radius, whereas the result given by (3.35)–(3.37) predicts a dependence on the drop radius. The analysis given in §§ 4.1 and 4.2 shows that, for given κ_i and κ_e, with an increase in the drop radius, a, the normalized drop deformation $\delta d/\delta W$ changes from the constant value given by (1.3) (OTAM theory) to the constant value given by (1.4) (Taylor's theory). For a given pair of liquids forming the contacting phases, the direction of changes in $\delta d/\delta W$ with a would depend on the difference between the OTAM and Taylor limits.

The difference between the Taylor and OTAM limits, $\delta d_{Taylor} - \delta d_{OTAM}$, is evaluated using (1.3) and (1.4). After minor transformations, one obtains

$$\frac{\delta d_{Taylor} - \delta d_{OTAM}}{\delta W} = \frac{27(H-S)}{16(H+2)^2(S+2)^2} \times \left[H(2S+1) + \frac{(16+19M)S^2 + (79+91M)S + 4 + 16M}{15(1+M)}\right]. \tag{5.4}$$

Since all the parameters H, S and M are positive, equation (5.4) leads to the following conclusion:

$$\left.\begin{array}{ll} \delta d_{OTAM} < \delta d_{Taylor} & \text{when} \quad H > S, \\ \delta d_{OTAM} > \delta d_{Taylor} & \text{when} \quad H < S. \end{array}\right\} \tag{5.5}$$

Although on increasing the drop radius, a, the drop deformation goes from the OTAM to Taylor's limit, the direction of the $\delta d/\delta W$ change is dependent on the ratio H/S. Thus, with an increase in a, one can expect the following behaviour. When $H > S$, $\delta d/\delta W$, increases from the OTAM limit to Taylor's limit. However, when $H < S$, $\delta d/\delta W$ decreases from the OTAM limit to Taylor's limit.

Having analysed the available data on parameters of different liquids, we did not find any exceptions to the following rule:

$$\left.\begin{array}{lll} \text{if} \quad S > 1 & \text{then} & H > S, \\ \text{if} \quad S < 1 & \text{then} & H < S. \end{array}\right\} \tag{5.6}$$

Thus, in the case of a more polar internal liquid ($S > 1$), one can expect the normalized drop deformation, $\delta d/\delta W$, to be an increasing function of the drop radius, a. The fact that $\delta d_{OTAM} < \delta d_{Taylor}$ and the fact that a prolate shape is always produced through the OTAM theory, lead to the conclusion that a prolate shape would always be produced for $S > 1$ regardless of the value of the drop radius a.

When the external liquid is more polar ($S < 1$), the value of $\delta d/\delta W$ is a decreasing function of the drop radius, a. In this case $\delta d_{OTAM} > \delta d_{Taylor}$. Therefore, with increasing drop radius, the drop deformation δd decreases from δd_{OTAM} to δd_{Taylor}.

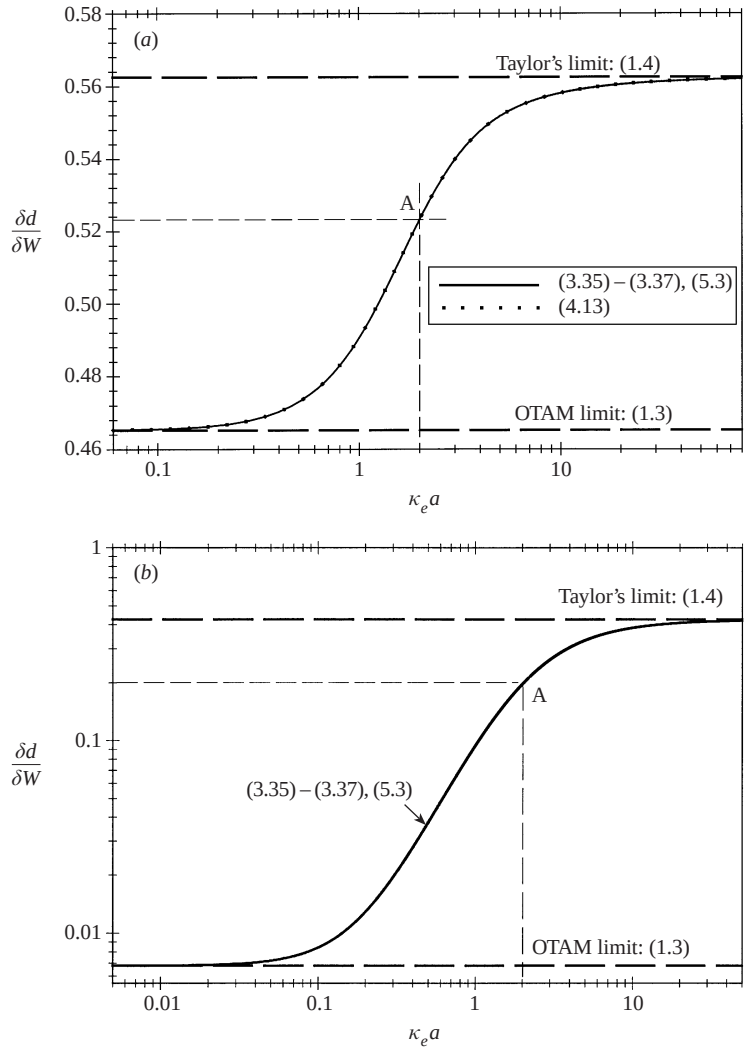

FIGURE 4. $S > 1$. Normalized drop deformation, $\delta d/\delta W$, as an increasing function of (*a*) $\kappa_e a$ for deionized water drop in silicone oil, $H = 10^8$, $S = 31.1$, $M = 0.001$; (*b*) $\kappa_i a$ for castor oil drop in silicone oil, $H = 10$, $S = 1.37$, $M = 0.11$.

Thus, for $S < 1$, a prolate shape is observed for all values of a if and only if Taylor's limit yields a prolate shape ($\delta d_{Taylor} > 0$). When Taylor's limit yields the oblate shape ($\delta d_{Taylor} < 0$), by increasing the drop radius, one can change from a prolate shape to an oblate shape.

The behaviour of the normalized drop deformation $\delta d/\delta W$ as a function of the drop radius is illustrated in figures 4 and 5. The plots were obtained for systems whose parameters H, S and M were given in Ha & Yang (2000). The solid curves in all plots display the function given by (3.35)–(3.37) and (5.3). By specifying values for H, S and M, equation (5.10) provides the ratio $\kappa_i a/\kappa_e a$. Consequently, by varying either $\kappa_i a$ or $\kappa_e a$, the other parameter is determined using (5.3).

Parameters of systems with $S > 1$ were employed to obtain the curves in figures 4(*a*) and 4(*b*). In these plots, due to (5.5) and (5.6), with an increase in the drop radius, the

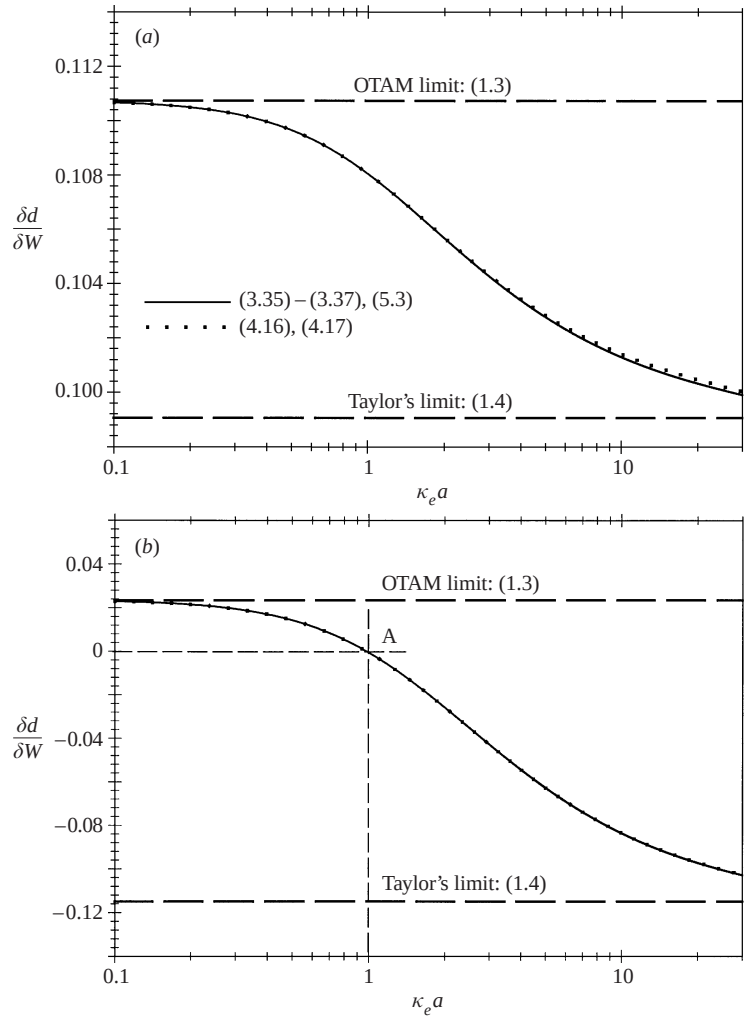

FIGURE 5. $S < 1$. Normalized drop deformation, $\delta d/\delta W$, as a decreasing function of $\kappa_e a$ for (a) silicone oil drop in a glycerine–methanol mixture, $H = 10^{-4}$, $S = 0.078$, $M = 62.5$; (b) silicone oil drop in castor oil with triton, $H = 10^{-4}$, $S = 0.491$, $M = 5$.

normalized drop deformation increases from the value given by the OTAM limit to Taylor's limit. The OTAM theory predicts only prolate shapes, $\delta d_{OTAM} \geqslant 0$. Therefore, when $S > 1$, one can observe only a prolate shape.

The curves presented in figure 4(a) correspond to a system of deionized water in a silicone oil, so there is a sharp difference in the dielectric permitivities and conductivities, namely, $S = 31.1$ and $H = 10^8$. For the chosen parameters, the variation of $\delta d/\delta W$ is confined within a relatively narrow range which is defined by the closeness of the OTAM and Taylor's limits. For the parameters employed in figures 4(a). Taylor's limit almost coincides with the common limit given by (1.5), $\delta d_{Taylor} \approx \delta d_{common}$. The OTAM limit can be evaluated as $\delta d_{OTAM} = \delta d_{common}(S-1)^2/(S+2)^2 \approx 0.8\delta d_{common}$.

The Debye parameter κ_i for the deionized water takes a value of order $10^7\ \mathrm{m}^{-1}$. It is clear from figure 4(a), that for the deionized water drops with $a \approx 2 \times 10^{-7}$ m (point A, $\kappa_i a = 2$), Taylor's equation (1.4) overpredicts the deformation by about 13%. For the same drop radius, the OTAM result (1.3) underpredicts the drop deformation by

9%. Deionized water drops with $a \geqslant 2 \times 10^{-6}$ m ($\kappa_i a \geqslant 20$) are deformed according to Taylor's equation (1.4). To be described by the OTAM expression (1.3) with an accuracy about 1%, the deionized water drop should have $a \leqslant 5 \times 10^{-8}$ m.

For the case of $S = 31.1$ and $H = 10^8$ (figure 4*a*), the relatively simple equation (4.13), which was derived in § 4.3 for the particular case of a conducting drop in a perfect dielectric liquid, yields excellent agreement with the exact result given by (3.35)–(3.37). Such an agreement is quite remarkable as $\kappa_e a$ was set to zero in deriving (4.13) whereas it has a value as high as unity.

A substantial variation in the normalized drop deformation with the drop radius can be observed for the case of $S > 1$ provided that the permitivities and conductivities do not differ as sharply as in the previous example. The example given in figure 4(*b*) illustrates the behaviour of a castor oil drop in a silicone oil medium, $S = 1.37$ and $H = 10$. For this system the Taylor's limit exceeds the OTAM limit by about 60 times. Using (5.3), one can evaluate that $\kappa_{SO} \approx \kappa_w (S/HM)^{1/2} \approx 2 \times 10^{-2}\ \kappa_w \approx 2 \times 10^5\ \mathrm{m}^{-1}$, where κ_{SO} and κ_w are the Debye parameters of the silicone oil and the deionized water, respectively. Accordingly, in figure 4(*b*), the parameter $\kappa_e a = \kappa_{SO} a \approx 2$ (point A) corresponds to drops having a radius of $a \approx 10^{-5}$ m. For $a \approx 10^{-5}$ m, the present theory yields a drop deformation which is approximately half that predicted by Taylor's theory and 30 times more than that given by the OTAM theory.

In figures 5(*a*) and 5(*b*), where $\delta d/\delta W$ is represented as a function of $\kappa_e a$, the curves are for $S < 1$. Accordingly, with an increase in a, the value of $\delta d/\delta W$ decreases from the OTAM limit to Taylor's limit, which is lower than the OTAM limit. The curves obtained using (3.35)–(3.37) and (5.3) coincide with the curves obtained using (4.16) and (4.17) (a perfect dielectric drop in a conducting medium).

In the case of $S < 1$, Taylor's expression (1.4) predicts both prolate ($\delta d_{Taylor} > 0$) and oblate ($\delta d_{Taylor} < 0$) shapes. Rearranging (1.4) yields

$$S < 5(H-1)^2 \frac{1+M}{16+19M} + H \quad \text{(prolate shape,} \quad \delta d_{Taylor} > 0), \tag{5.7}$$

$$S > 5(H-1)^2 \frac{1+M}{16+19M} + H \quad \text{(oblate shape,} \quad \delta d_{Taylor} < 0). \tag{5.8}$$

Figures 5(*a*) and 5(*b*) illustrate the behaviour of systems governed by conditions (5.7) and (5.8). In figure 5(*b*), at sufficiently small drop radius a, the drop has a prolate shape, $\delta d > 0$, but with an increase in radius, the drop reaches the state of $\delta d < 0$, i.e. the drop takes an oblate shape. Point A in figure 5(*b*) corresponds to a spherical drop shape.

6. Conclusions

(i) The main result of the present theory is given by equations (3.35)–(3.37) which yield the expression for the normalized drop deformation $\delta d/\delta W$, where $\delta W = \varepsilon_0 \varepsilon_e a (\delta E)^2/\gamma$. The expression derived for $\delta d/\delta W$ is valid for arbitrary Reynolds number in the limiting case of $\delta E \to 0$ and is represented by (3.35)–(3.37) as a function of five arguments. The first three arguments, $H = \sigma_i/\sigma_e$, $S = \varepsilon_i/\varepsilon_e$, and $M = \eta_i/\eta_e$, were employed in Taylor's (1966) model. The other two arguments, $\kappa_e a$ and $\kappa_i a$, are the ratios of the particle radius, a, to the Debye lengths, κ_e^{-1} and κ_i^{-1}, of the outer and inner liquids, respectively.

(ii) For perfect dielectrics ($\kappa_e a \to 0$ and $\kappa_i a \to 0$ simultaneously), the main result, which is given by (3.35)–(3.37), is transformed into the expression obtained earlier by

O'Konski & Thacher (1953) and Allan & Mason (1962). At the limiting transitions given either by $\kappa_e a \to \infty$ ($\kappa_i a$ is an arbitrary constant) or by $\kappa_i a \to \infty$ ($\kappa_e a$ is an arbitrary constant), the result given by (3.35)–(3.37) is transformed into Taylor's (1966) expression for leaky dielectrics.

(iii) For a conducting drop in a perfect dielectric ($\kappa_e a \to 0$), the result given by (3.35)–(3.37) is reduced to the much simpler expression (4.13) which can describe a conducting drop in a perfect dielectric medium for an arbitrary set of charge carriers.

(iv) For a perfect dielectric drop in a conducting medium ($\kappa_i a \to 0$), the result given by (3.35)–(3.37) is transformed into (4.16) and (4.17).

(v) According to (3.35)–(3.37), for constant values of H, S and M the normalized drop deformation, $\delta d/\delta W$, changes with an increase in the drop radius a, from the value obtained earlier by O'Konski & Thacher (1953) and Allan & Mason (1962), to the value given by Taylor's (1966) theory. When $S > 1$ the value of $\delta d/\delta W$ is an increasing function of a. If $S < 1$, $\delta d/\delta W$ is a decreasing function of a. In the case of $S < 1$, when the condition given by (5.8) is satisfied, increasing the drop radius results in the drop shape changing from prolate to oblate.

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