Dielectric Response of a Dilute Suspension of Spheres with Thin Double Layers in an Asymmetric Electrolyte

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The low-frequency dielectric response of a suspension of spherical particles surrounded by thin double layers has been studied and the analysis of Dukhin and Shilov has been extended to asymmetric electrolytes. In addition to the cases of constant surface charge density and of constant surface potential, the case in which changes in the surface charge density are determined by changes in the surface potential according to a first-order kinetic equation has also been examined.

It is well known that the dielectric response of a colloidal suspension can be quite different from that of the suspending electrolyte alone, especially at low frequencies. Typical examples are the experiments of Schwan et al.[1] and of Ballario et al.[2] on suspensions of polystyrene particles. Relative permittivities of 1000 or more were measured at low frequencies. (See Chou and Shah[3] for references to other experiments.) Standard Maxwell–Wagner analysis for a two-phase material is unable to explain such results, which are thought to be caused by the charged double layers surrounding the particles. Early analyses[4,5] ascribed frequency-dependent properties such as surface conductivity and capacity to the double layers. Dukhin and Shilov[6] studied the flux of ions in thin double layers and the surrounding symmetric electrolyte and successfully fitted their predictions to the experimental results. Similar analyses have been presented by Chew and Sen[7] and by Fixman.[8,9] Full numerical solutions over a range of double-layer thicknesses have been obtained by DeLacey and White,[10] while O'Brien[11] has studied the limit of low ζ potentials. Here we consider thin double layers and asymmetric electrolytes, following O'Brien[12] and Hinch and Sherwood.[13] We examine the dominant role played by the counter-ions of highest valence. It is also straightforward to compare the effect of various boundary conditions at the surface of the charged particle.

Our analysis is similar to that of Dukhin and Shilov.[6] The frequency is assumed to be sufficiently low so that within one cycle the ions can diffuse a distance comparable to the particle radius a. Thus, to a first approximation, the thin double layer is quasi-static. We obtain the form of the solution outside the double layer and must then determine the constants in this solution, in particular the effective polarization of the spherical particle. This is achieved by studying the ion flux

balances obtained by integration through the double layer. At very high surface potentials the tangential flux of the counter-ions with the highest valence cannot be ignored and is evaluated from our knowledge of the structure of the double layer.

GOVERNING EQUATIONS

The suspending electrolyte contains I species of ions with valences z^i, mobilities ω^i and number densities $n^i(r, t)$. The electric potential ϕ and the charge density ρ are related by Poisson's equation

$$\nabla \cdot \varepsilon \nabla \phi = -\rho = -\sum_i ez^i n^i$$

where the permittivity $\varepsilon = \varepsilon_w$ in the electrolyte and we assume that ε is negligibly small inside the particle. If the imposed oscillating electric field has magnitude E and frequency σ, then, in spherical polar coordinates, we require

$$\phi \sim -E \exp (i\sigma t) r \cos \theta \quad \text{as } r \to \infty.$$

The boundary condition at the surface of the particle has the form

$$\phi = \zeta \quad \text{on } r = a \text{ when } E = 0.$$

When $E \neq 0$ we initially assume either a constant surface charge density

$$\left[\varepsilon \frac{\partial \phi}{\partial r} \right]_{a^-}^{a^+} \quad \text{unchanged}$$

or a constant surface potential

$$\phi \quad \text{unchanged on } r = a.$$

Later we shall give an intermediate condition representing relaxation of the surface charge density.

The ions are convected by the fluid velocity u and move relative to the fluid under the influence of electric and thermodynamic forces. The ion-conservation equation becomes

$$\frac{\partial n^i}{\partial t} + \nabla \cdot [un^i - \omega^i(ez^i n^i \nabla \phi + kT \nabla n^i)] = 0$$

with boundary condition

$$n^i \to n_\infty^i \quad \text{as } r \to \infty$$

where

$$\sum_i z^i n_\infty^i = 0$$

for electrical neutrality of the bulk electrolyte. We initially take the boundary condition at the surface of the particle to be

$$n \cdot [un^i - \omega^i(ez^i \nabla \phi + kT \nabla n^i)] = 0 \quad \text{on } r = a$$

where n is the normal to the particle surface. This requires any change in the surface charge (in the case of constant surface potential) to be provided by the free movement of charges within the particle. Later this condition will be modified to permit the ions to supply this change in the surface charge.

At typical frequencies and for small colloidal particles we can neglect fluid inertia. The motion of the fluid is therefore governed by the Stokes equations:

$$0 = -\nabla p + \mu \nabla^2 \mathbf{u} - \rho \nabla \phi$$

$$\nabla \cdot \mathbf{u} = 0$$

where p is the pressure and μ is the viscosity of the suspending fluid. We take the boundary conditions to be

$$\mathbf{u} \to 0 \quad \text{as } r \to \infty$$

$$\mathbf{u} = 0 \quad \text{on } r = a.$$

Note that we have assumed that a small force acts on the particle to keep it stationary. In reality this force is not applied. The particle will therefore move, as in electrophoresis, with a velocity equal to force times mobility. For a sphere with thin double layers the mobility is $(6\pi\mu a)^{-1}$, with very small corrections due to the double layer.

The imposed electric field $E \exp(i\sigma t)$ is assumed weak compared with the natural electric fields within the thin double layer. Thus we expand all variables in the above equations as an unperturbed term (with subscript 0) and a perturbation (subscript 1) linear in $E \exp(i\sigma t)$, e.g.

$$\phi = \phi_0 + \phi_1.$$

We ignore corrections which are non-linear in E and the consequent higher harmonics.

OUTSIDE THE DOUBLE LAYER

There is no fluid motion when there is no imposed field ($\mathbf{u}_0 = 0$), so the linearized form of the ion flux equations is

$$\frac{\partial n_1^i}{\partial t} + \nabla \cdot \{\mathbf{u}_1 n_0^i - \omega^i [ez^i(n_1^i \nabla \phi_0 + n_0^i \nabla \phi_1) + kT\nabla n_1^i]\} = 0.$$

Outside the thin double layer, which has thickness

$$\kappa^{-1} = (\varepsilon_w kT / \sum_i e^2 z^{i2} n_\infty^i)^{1/2}$$

the undisturbed electrolyte is unaffected by the double layer. Hence

$$\phi_0 = 0 \quad \text{and} \quad n_0^i = n_\infty^i.$$

Now n_1^i is proportional to $\exp(i\sigma t)$, so freely interchanging n_1^i with its Fourier amplitude and using $\nabla \cdot \mathbf{u} = 0$, the ion-flux equation becomes

$$i\sigma n_1^i - \omega^i (ez^i n_\infty^i \nabla^2 \phi_1 + kT\nabla^2 n_1^i) = 0.$$

Poisson's equation gives

$$ez^i n_\infty^i \nabla^2 \phi_1 = kT\kappa^2 z^i n_\infty^i \sum_j z^j n_1^j / \sum_j (z^j)^2 n_\infty^j.$$

Hence the general solution for the number densities outside the double layer is a linear combination of the eigensolutions with a first harmonic variation

$$n_1^i = \sum_{k=1}^{I} c_k A_k^i \left(\frac{a^2}{r^2} \frac{1 + \lambda_k r}{1 + \lambda_k a} \right) \exp[-\lambda_k(r-a)] \cos\theta \exp(i\sigma t)$$

with eigenvalue λ_k and eigenvector A_k^i satisfying

$$\left(\frac{i\sigma}{\omega^i kT} - \lambda^2\right)A^i + \frac{\kappa^2 z^i n_\infty^i \sum_j z^j A^j}{\sum_j z^{j2} n_\infty^j}.$$

Now we restrict the frequency to be not very high, so that the distance the ions diffuse during an oscillation is much larger than the double layer thickness, i.e. $(\omega^i kT/\sigma)^{1/2} \gg \kappa^{-1}$. In this case there is one eigenvalue $\lambda_1^2 \approx \kappa^2$ and $A_1^i \propto z^i n_\infty^i$. This is merely the linearized double layer. If all the ions have the same mobility, the remaining eigensolutions are $\lambda^2 = i\sigma/\omega kT$ with $\sum z^j A^j = 0$, i.e. the eigensolutions represent neutral charge clouds. In general, though, ω^i varies between ion species, so we adopt the normalization

$$\sum_j z^j A_k^j = \lambda_k^2 \kappa^{-2} \sum_j z^{j2} n_\infty^j, \qquad k = 2, 3, \dots, I.$$

Then

$$A_k^i = z^i n_\infty^i \lambda_k^2 \left/ \left(\lambda_k^2 - \frac{i\sigma}{\omega^i kT}\right)\right.$$

and we see that the eigensolutions are non-neutral at $\mathcal{O}(\lambda_k/\kappa)^2$. Substituting this expression for A into the preceeding normalization yields a polynomial in λ^2 of degree $I-1$ for $\lambda_2, \dots, \lambda_I$. For an electrolyte with just two species of ions

$$\lambda_2^2 \approx \frac{i\sigma}{kT}\left(\frac{z^2}{\omega^1} - \frac{z^1}{\omega^2}\right) \left/ (z^2 - z^1)\right..$$

This is exact if $\omega^1 = \omega^2$, and holds more generally for our restricted frequency range. Similarly

$$z^1 A^1 = -z^2 A^2 = \frac{[(z^2/\omega^1) - (z^1/\omega^2)]z^1 n_\infty^1}{(1/\omega^1) - (1/\omega^2)}$$

where we have used the neutrality condition $z^1 n_\infty^1 + z^2 n_\infty^2 = 0$. The $\mathcal{O}(\lambda/\kappa)^2$ degree of non-neutrality of these eigensolutions, extending over distances $\mathcal{O}(\lambda^{-1})$ which are large compared with the double-layer thickness κ^{-1}, results in an $\mathcal{O}(1)$ change in the potential. Thus outside the double layer the electric potential takes the form

$$\phi_1 = -\left[E(r + Pa^3/r^2) + \frac{kT}{e}\sum_{k=2}^{I} c_k\left(\frac{a^2}{r^2}\frac{1+\lambda_k r}{1+\lambda_k a}\right)\exp\left(-\lambda_k(r-a)\right)\right]\cos\theta\exp(i\sigma t)$$

where the constant P is the effective polarization of the particle together with its double layer. The evaluation of P is the object of this study.

INTEGRATED FLUX BALANCE ACROSS THE DOUBLE LAYER AT MODERATE POTENTIALS

We can obtain the unknown constants $c_2, c_3, \dots c_I$ and P in the solution outside the double layer without a full determination of the solution within the double layer. Integrating through the double layer the equations for the perturbed ion-

number densities we find the integrated flux balances

$$i\sigma \int_{dl} n_1^i \, dr + \int_{dl} \nabla \cdot \mathbf{u}_1 n_0^i \, dr - \int_{dl} \nabla_t \cdot \omega^i (ez^i n_0^i \nabla_t \phi_1 + kT\nabla_t n_1^i) \, dr$$

$$-\omega^i \left(ez^i n_\infty^i \frac{\partial \phi}{\partial r} \bigg|_{dl+} + kT \frac{\partial n_1^i}{\partial r} \bigg|_{dl+} \right) = 0$$

where dl stands for the double layer, dl+ stands for just outside the double layer and ∇_t is the tangential differential operator. In obtaining the above flux balances we have used the no-flux boundary conditions on $r = a$ and the results

$$\nabla_t \phi_0 = 0 \qquad \text{everywhere}$$

$$\left. \begin{array}{l} \dfrac{\partial \phi_0}{\partial r} = 0 \\[2ex] n_0^i = n_\infty^i \end{array} \right\} \quad \text{outside the double layer.}$$

At moderate potentials (to be defined later) order-of-magnitude arguments allow us to neglect the integral terms in the above flux balances. Since

$$n_1^i = \mathcal{O}(n_\infty^i eEa/kT)$$

the first integral

$$i\sigma \int n_1^i \, dr = \mathcal{O}(\sigma n_\infty^2 eEa/kT\kappa).$$

This must be compared with a leading order term in the flux balance

$$\omega^i ez^i n_\infty^i \frac{\partial \phi_1}{\partial r} \bigg|_{dl+} = \mathcal{O}(\omega^i en_\infty^i E).$$

The ratio of these two terms is

$$\mathcal{O}\left(\frac{\sigma a^2}{\omega^i kT} \frac{1}{a\kappa} \right).$$

Since we are assuming $\sigma = \mathcal{O}(\omega kT/a^2)$, this is small.

Now the fluid motion is driven by electrostatic forces $\mathcal{O}(en_\infty E)$, which, acting across the double layer, induce a tangential velocity $\mathcal{O}(en_\infty E/\mu\kappa^2)$. The tangential divergence of this tangential velocity produces a radial component of the velocity $\mathcal{O}(en_\infty E/\mu a\kappa^3)$. Thus we estimate the magnitude of the second neglected integral

$$\int_{dl} \nabla \cdot \mathbf{u}_1 n_0^i \, dr = \mathcal{O}(en_\infty^2 E/\mu a\kappa^3)$$

and the ratio of this to the leading order term is

$$\mathcal{O}(n_\infty/\omega^i \mu a\kappa^3) = \mathcal{O}\left(\frac{\varepsilon_w kT}{\omega^i e^2 \mu} \frac{1}{a\kappa} \right).$$

Now the first factor is a property of the electrolyte. For water at normal temperatures and ions with mobility $4 \times 10^{11} \text{ kg s}^{-1}$ this factor is 0.26, and hence the second neglected integral is smaller than the retained terms by the factor $(a\kappa)^{-1}$.

Finally for the third integral, the tangential component of the electric field $\nabla_t \phi_1$ has magnitude E and so

$$\int_{dl} \nabla_t \cdot \omega^i (ez^i n_0^i \nabla_t \phi_1 + kT\nabla_t n_1^i) \, dr = \mathcal{O}(\omega^i e n_\infty^i E / a\kappa)$$

which, like the other two integrals, is $\mathcal{O}(a\kappa)^{-1}$ smaller than the terms retained.

Neglecting the three integral terms, we substitute into the simplified integrated flux balances the forms of ϕ_1 and n_1^i outside the double layer and obtain

$$eE(1-2P) + \frac{2kT}{a} \sum_{k=2}^{I} c_k \left(\frac{i\sigma}{\lambda_k^2 \omega^i kT - i\sigma}\right) \left(\frac{1 + \lambda_k a + \frac{1}{2}\lambda_k^2 a^2}{1 + \lambda_k a}\right) = 0.$$

Thus we have determined the constants at moderate potentials

$$P = 1/2 \quad \text{and} \quad c_k = 0, \qquad k = 2, 3, \ldots, I.$$

These arguments, however, break down at very high surface potentials ζ. The counter-ions with highest valence then become so numerous that the above estimates need correcting. We label these ions as the Ith species. Their number density close to the particle is enhanced by the factor $\exp(-ez^I \zeta / kT)$, where $ez^I \zeta < 0$. This high density of counter-ions effectively screens the high surface potential ζ to a moderate value $\mathcal{O}(4kT/ez^I)$ over a small fraction of the double layer of thickness $\kappa^{-1} \exp(ez^I \zeta / 2kT)$. Thus all the above estimates for the neglected integrals need correction in the case of the special Ith species by a factor $\exp(-ez^I \zeta / 2kT)$, which is the enhanced number density multiplied by the distance over which it is integrated. We therefore conclude that the result

$$P = 1/2$$

is only appropriate at moderate potentials satisfying

$$\exp\left(\tfrac{1}{2}|ez^I \zeta|kT\right) \ll a\kappa.$$

We now proceed to higher potentials and examine the internal structure of the double layer in order to evaluate the three integrals.

THE UNDISTURBED DOUBLE LAYER

When no external electric field is applied, the ions are in a Maxwell–Boltzmann distribution

$$n_0^i = n_\infty^i \exp(-ez^i \phi_0 / kT).$$

Thus Poisson's equation for the undisturbed potential in the thin double layer is

$$\varepsilon_w \frac{d^2\phi_0}{dr^2} = -\sum_i ez^i n_\infty^i \exp(-ez^i \phi_0 / kT).$$

This can be integrated once:

$$\tfrac{1}{2}\varepsilon_w \left(\frac{d\phi_0}{dr}\right)^2 = \sum_i kTn_\infty^i [\exp(-ez^i \phi_0 / kT) - 1].$$

A further integration is well known for a symmetric electrolyte:

$$\phi_0 = \frac{2kT}{ez^I} \ln\left(\frac{\alpha - \exp[-(r-a)\kappa]}{\alpha + \exp[-(r-a)\kappa]}\right)$$

where

$$\alpha = \frac{\exp(-ez^I\zeta/2kT)+1}{\exp(-ez^I\zeta/2kT)-1}.$$

In the case of a general asymmetric electrolyte, however, it is not possible to find an explicit expression for $\phi_0(r)$. At low potentials we may linearize the Poisson–Boltzmann equation, while at high surface potentials we can obtain an expression for $\phi_0(r)$ in the inner part of the double layer. In regions of high potential $|e\phi_0/kT| \gg 1$ the counter-ions with the highest valency will be more dense than any other ion by a factor $\exp|e(z^I-z^i)\phi_0/kT|$. Hence in this region

$$\tfrac{1}{2}\varepsilon_w\left(\frac{d\phi_0}{dr}\right)^2 \sim kTn^I_\infty \exp(-ez^I\phi_0/kT).$$

Integrating, we find

$$\phi_0 \sim \frac{2kT}{ez^I} \ln\left[\exp(ez^I\zeta/2kT)+\kappa_I(r-a)\right]$$

where κ_I^{-1} is a Debye–Hückel distance based on the Ith species alone:

$$\kappa_I^2 = e^2 z^{I2} n^I_\infty / 2\varepsilon_w kT.$$

The restriction that the potential be high restricts this solution to the inner part of the double layer

$$r - a = \mathcal{O}[\kappa_I^{-1} \exp(ez^I\zeta/2kT)].$$

THE PERTURBATION ION DENSITY AND POTENTIAL INSIDE THE DOUBLE LAYER

To leading order the perturbed ion density n^i_1 is governed by the radial flux balance

$$-ez^i\left(n^i_1 \frac{\partial\phi_0}{\partial r}+n^i_0 \frac{\partial\phi_1}{\partial r}\right)-kT\frac{\partial n^i_1}{\partial r}=0.$$

Here we have applied the no-flux boundary condition, having first assumed that the double layer is quasistatic and that the fluid motion is negligible. Using the Maxwell–Boltzmann distribution for $n^i_0(r)$ we can integrate the radial flux balance to yield, within the double layer,

$$n^i_1(r) = \exp(-ez^i\phi_0/kT)\left(n^i_1(+)-n^i_\infty \frac{ez^i}{kT}[\phi_1-\phi_1(+)]\right)$$

where $n^i_1(+)$ and $\phi_1(+)$ are the values just outside the double layer

$$n^i_1(+) = \sum_{k=2}^I c_k A^i_k \cos\theta \exp(i\sigma t)$$

and

$$\phi_1(+) = -\left(Ea(1+P)+\frac{kT}{e}\sum_{k=2}^I c_k\right)\cos\theta \exp(i\sigma t).$$

Note that the above solution for n^i_1 merely represents a Maxwell–Boltzmann distribution for the combined densities

$$n^i_0 + n^i_1 \propto \exp[-ez^i(\phi_0+\phi_1)/kT]$$

within the double layer, ignoring terms $\mathcal{O}(E)^2$. Substituting this perturbed ion density into Poisson's equation gives the equation governing the perturbed potential

$$\varepsilon_w \frac{\partial^2 \phi_1}{\partial r^2} = -\sum_i ez^i n_1^i(+) \exp\left(-ez^i\phi_0/kT\right)$$

$$+\sum_i \frac{e^2 z^{i2}}{kT} n_\infty^i [\phi_1 - \phi_1(+)] \exp\left(-ez^i\phi_0/kT\right).$$

We look for a solution in the form

$$\phi_1 = \phi_1(+) + \frac{d\phi_0}{dr} f(r)$$

where

$$\frac{d^2 f}{dr^2}\frac{d\phi_0}{dr} + 2\frac{df}{dr}\frac{d^2\phi_0}{dr^2} = -\sum_i \frac{ez^i n_1^i(+)}{\varepsilon_w} \exp\left(-ez^i\phi_0/kT\right)$$

which integrates to

$$\frac{df}{dr}\left(\frac{d\phi_0}{dr}\right)^2 = B_1 + \sum_i \frac{kTn_1^i(+)}{\varepsilon_w} [\exp\left(-ez^i\phi_0/kT\right) - 1].$$

The constant of integration B_1 must be zero if f is not to grow like $\exp(2\kappa r)$ at the edge of the double layer. Using our previous expression for $(d\phi_0/dr)^2$ we obtain

$$f = B_2 + \frac{1}{2}\int_a^r \frac{\sum_i n_1^i(+)[\exp\left(-ez^i\phi_0/kT\right) - 1]}{\sum_i n_\infty^i [\exp\left(-ez^i\phi_0/kT\right) - 1]}$$

and within the inner part of the double layer

$$f \sim B_2 + \frac{1}{2}\frac{n_1^I(+)(r-a)}{n_\infty^I}.$$

The constant of integration B_2 is determined by the boundary condition at $r = a$. For the constant potential condition

$$B_2 = -\phi_1(+)\left/\frac{d\phi_0}{dr}\right|_{r=a}$$

while for constant surface charge density

$$B_2 = -\frac{1}{2}\frac{d\phi_0}{dr}\bigg|_{r=a} \sum_i n_1^i(+)\left[\exp\left(-ez^i\zeta/kT\right) - 1\right]$$

$$\div \frac{d^2\phi_0}{dr^2}\bigg|_{r=a} \sum_i n_\infty^i \left[\exp\left(-ez^i\zeta/kT\right) - 1\right].$$

At high surface potentials, with the inner part of the double layer dominated by the counter-ions with the highest valency, the above expressions for B_2 become

$$B_2 \sim -\tfrac{1}{2}\kappa_I^{-1}\frac{ez^I}{kT}\phi_1(+)\exp\left(ez^I\zeta/2kT\right) \quad \text{for constant potential}$$

and

$$B_2 \sim \tfrac{1}{2}\kappa_I^{-1}\frac{n_1^I(+)}{n_\infty^I}\exp\left(ez^I\zeta/2kT\right) \quad \text{for constant charge.}$$

THE FIRST INTEGRAL IN THE FLUX BALANCE

We are now in a position to evaluate the first of the neglected integrals in the flux balance. For the special Ith species

$$i\sigma \int_{dl} n_1^I \, dr = i\sigma \int_{dl} \left(n_1^I(+) - \frac{n_\infty^I ez^I}{kT} \frac{d\phi_0}{dr} f \right) \exp\left(-ez^I \phi_0 / kT \right) dr$$

$$= -i\sigma [n_\infty^I B_2 \exp\left(-ez^I \zeta / kT \right) - \tfrac{1}{2} n_1^I(+) \kappa_I^{-1} \exp\left(-ez^I \zeta / 2kT \right)]$$

integrating by parts and using the form for f within the inner part of the double layer. Substituting the values for B_2 we have, for the constant potential boundary condition,

$$i\sigma \int_{dl} n_1^I \, dr = -\tfrac{1}{2} i\sigma z^I n_\infty^I \kappa_I^{-1} \exp\left(-ez^I \zeta / 2kT \right) \cos\theta \exp(i\sigma t)$$

$$\times \left(\frac{eEa(1+P)}{kT} - \sum_{k=2}^{I} c_k \left(\frac{i\sigma}{\lambda_k^2 \omega^I kT - i\sigma} \right) \right)]$$

and for the constant charge boundary condition

$$i\sigma \int_{dl} n_1^I \, dr = e \left[i\sigma \kappa_I^{-1} n_\infty \frac{ez^I}{kT} Ea \exp\left(-ez^I \zeta / 2kT \right) \right].$$

FLUID MOTION IN THE DOUBLE LAYER

The radial component of the momentum equation is to leading order a balance between the radial pressure gradient and the strong radial component of the electric force

$$\frac{\partial p}{\partial r} = -\rho_1 \frac{\partial \phi_0}{\partial r} - \rho_0 \frac{\partial \phi_1}{\partial r}$$

which integrates once to yield

$$p = \sum_i kT n_1^i(+) [\exp\left(-ez^i \phi_0 / kT \right) - 1] - \sum_i ez^i n_\infty^i \exp\left(-ez^i \phi_0 / kT \right) \frac{d\phi_0}{dr} f.$$

Substituting this into the tangential component of the momentum equation, we derive an equation for the tangential component of velocity u_θ valid within the double layer

$$\mu \frac{\partial^2 u_\theta}{\partial r^2} = \frac{1}{a} \frac{\partial p}{\partial \theta} + \rho_0 \frac{1}{a} \frac{\partial \phi_1}{\partial \theta}$$

$$= \sin \exp(i\sigma t) \left[\frac{-kT}{a} \sum_{i,k} c_k A_k^i [\exp\left(-ez^i \phi_0 / kT \right) - 1] \right.$$

$$\left. + \left(E(1+p) + \frac{kT}{ae} \sum_k c_k \right) \sum_i ez^i n_\infty^i \exp\left(-ez^i \phi_0 / kT \right) \right].$$

While the second term can be integrated twice for a contribution to u_θ of

$$\sin\theta \exp(i\sigma t) \left(E(1+P) + \frac{kT}{ae} \sum_k c_k \right) \varepsilon_w \mu^{-1} [\zeta - \phi_0(r)]$$

the first term does not integrate so simply. If we restrict attention to the inner part of the double layer, the two terms take a similar form, dominated by the Ith species of ions. Hence in the inner part of the double layer

$$u_\theta \sim \sin \theta \exp (i\sigma t) \varepsilon_w \mu^{-1} \left[E(1+P) - \frac{kT}{ae} \sum_k c_k \left(\frac{i\sigma}{\lambda_k^2 \omega^I kT - i\sigma} \right) \right] [\zeta - \phi_0(r)].$$

Integrating the equation for u_θ to the outside edge of the double layer, we find that the double layer produces an effective slip velocity $V \sin \theta \exp (i\sigma t)$ with

$$V = \varepsilon_w \mu^{-1} \left(\left[E(1+P) + \frac{kT}{ae} \sum_k c_k \right] \zeta - \frac{kT}{aez^I n_\infty^I} \sum c_k A_k^I [\zeta + \mathcal{O}(kT/e)] \right)$$

where the $\mathcal{O}(kT/e)$ term comes from all the species of ions and can be evaluated only if a full solution of the undisturbed potential ϕ_0 is known. The slip velocity induces a motion outside the double layer (satisfying the Stokes equation with no electric force and negligible radial motion into the double layer)

$$-\frac{1}{2} V \exp (i\sigma t) \left[\hat{z} \left(\frac{a}{r} + \frac{a^3}{r^3} \right) + r \frac{z}{r^2} \left(\frac{a}{r} - \frac{3a^3}{r^3} \right) \right]$$

where $\hat{z}$ is the unit vector E/E. This motion requires a force $-4\pi\mu a V \exp (i\sigma t)$ to hold the sphere fixed. Thus a free sphere in an oscillating electric field will move with velocity $\frac{2}{3} V \exp (i\sigma t)$.

THE SECOND INTEGRAL IN THE FLUX BALANCE

From the detailed form of the fluid motion in the inner part of the double layer we can now calculate the second integral in the flux balance for the special Ith species of ions. First we make some manipulations which eliminate the radial component of velocity:

$$\int_{dl} \nabla \cdot u_1 n_0^I \, dr = \int_{dl} \nabla \cdot u_1 (n_0^I - n_\infty^I) \, dr$$

because n_∞^I is a constant and $\nabla \cdot u_1 = 0$. The radial component then integrates to zero because $u_1 = 0$ on $r = a$ and $n_0^I - n_\infty^I \to 0$ at the edge of the double layer. Hence

$$\int_{dl} \nabla \cdot u_1 n_0^I \, dr = (a \sin \theta)^{-1} \frac{\partial}{\partial \theta} \sin \theta \int_{dl} u_\theta (n_0^I - n_\infty^I) \, dr$$

$$= -\cos \theta \exp (i\sigma t) \left(\frac{4\varepsilon_w kT n_\infty^I}{ez^I \mu a \kappa_I} \right) \left[E(1+P) \right.$$

$$\left. - \frac{kT}{ae} \sum_k c_k \left(\frac{i\sigma}{\lambda_k^2 \omega^I kT - i\sigma} \right) \right] \exp (-ez^I \zeta/2kT)$$

using the forms of u_θ and n_0^I in the inner part of the double layer.

THE THIRD INTEGRAL IN THE FLUX BALANCE

The final integral in the flux balance needs no additional investigations. Using our expressions for ϕ_1 and n_1^I, and for ϕ_0 within the inner part of the double layer,

we obtain

$$-\int_{dl} \nabla_t \cdot \omega^I (ez^I n_0^I \nabla_t \phi_1 + kT \nabla_t n_1^I)\, dr$$

$$= \frac{2\omega^I}{a^2} \int_{dl} [ez^I n_\infty^I \phi_1(+) + kT n_1^I(+)] \exp(-ez^I \phi_0/kT)\, dr$$

$$= -\cos\theta \exp(i\sigma t) \left(\frac{2\omega^I ez^I n_\infty^I}{a^2 \kappa_I}\right) \left[Ea(1+P) \right.$$

$$\left. - \frac{kT}{e} \sum_k c_k \left(\frac{i\sigma}{\lambda_k^2 \omega^I kT - i\sigma}\right) \right] \exp(-ez^I \zeta/2kT).$$

INTEGRATED FLUX BALANCE FOR HIGH SURFACE POTENTIALS

Bringing together the results for the integrals, we can now evaluate the integrated flux balances at arbitrary potentials. The balances for all but the special Ith species are unchanged from the form at moderate potentials, i.e. for $i = 1, 2, \ldots, I-1$:

$$eE(1-2P) + \frac{2kT}{a} \sum_{k=2}^{I} c_k \left(\frac{i\sigma}{\lambda_k^2 \omega^i kT - i\sigma}\right) \left(\frac{1 + \lambda_k a + \frac{1}{2}\lambda_k^2 a^2}{1 + \lambda_k a}\right) = 0.$$

Including the integrals which cannot be neglected at very high potentials, the integrated flux balance for the Ith species becomes, for the case of the constant potential boundary condition,

$$-\frac{\exp(-ez^I \zeta/2kT)}{a\kappa_I} \left[\frac{1}{2}\left(\frac{i\sigma a^2}{\omega^I kT}\right) + 2\left(1 + \frac{2\varepsilon_w kT}{e^2 z^{I2} \mu \omega^I}\right)\right]$$

$$\times \left[eE(1+P) - \frac{kT}{a} \sum_k c_k \left(\frac{i\sigma}{\lambda_k^2 \omega^I kT - i\sigma}\right) \right]$$

$$+ eE(1-2P) + 2\frac{kT}{a} \sum_{k=2}^{I} c_k \left(\frac{i\sigma}{\lambda_k^2 \omega^I kT - i\sigma}\right) \left(\frac{1 + \lambda_k a + \frac{1}{2}\lambda_k^2 a^2}{a + \lambda_k a}\right) = 0$$

and for the case of the constant charge boundary condition the same equation with the term $\frac{1}{2}i\sigma a^2/\omega^I kT$ omitted.

It is not possible to solve explicitly the system of linear equations for the constants $P, c_2, \ldots, c_I$ and so we must consider particular cases.

RESULTS FOR AN ELECTROLYTE WITH JUST TWO TYPES OF CHARGED IONS AND WITH THE CONSTANT POTENTIAL BOUNDARY CONDITIONS

If $I = 2$ there is just one mode outside the double layer. Solving the system of linear equations, we find for the case of the constant potential boundary condition

$$P = \tfrac{1}{2} - \tfrac{3}{2}\alpha\left(\frac{i}{4}\Sigma + \beta\right) \bigg/ \left[1 + \gamma + \alpha\left(\frac{i}{4}\Sigma + \beta\right)(1 + \gamma\delta)\right]$$

and

$$\tfrac{2}{3}V = \frac{\varepsilon_w \zeta E}{\mu} \left(1 - \frac{\alpha(i\Sigma/4 + \beta)\{1 + \delta\gamma[1 + \mathcal{O}(kT/e\zeta)]\}}{1 + \gamma + \alpha(i\Sigma/4 + \beta)(1 + \gamma\delta)}\right)$$

in which

$$\alpha = \frac{\exp\left(-ez^2\zeta/2kT\right)}{a\kappa_I}, \qquad \beta = 1 + \left(\frac{2\varepsilon_w kT}{e^2 z^{22}\mu\omega^2}\right), \qquad \gamma = \frac{-z^1\omega^1}{z^2\omega^2},$$

$$\delta = \frac{1 + \lambda a}{1 + \lambda a + \frac{1}{2}\lambda^2 a^2} \quad \text{and} \quad \Sigma = \frac{\sigma a^2}{\omega^2 kT}.$$

At low frequencies the polarization takes the form of a real constant part with a small imaginary part proportional to frequency

$$P \sim \frac{1}{2} - \left(\frac{3\alpha\beta}{2(1+\gamma)(1+\alpha\beta)}\right) - i\Sigma\,\frac{3\alpha}{8}\left(\frac{1 + \gamma + 2\beta^2\gamma\lambda^2 a^2/i\Sigma}{(1+\gamma)^2(1+\alpha\beta)^2}\right) \quad \text{as } \Sigma \to 0.$$

The real part of this low-frequency limit is $\frac{1}{2}$ at moderate potentials (low α) and decreases to the possibly negative value at very high potentials (high α). At very high potentials, the integrated tangential fluxes of the special Ith species would be so large, because they include the large factor α, that they must virtually vanish if they are to take part in the flux balance with other integrated fluxes, which are $\mathcal{O}(1)$. Thus we find that the tangential electric field [characterized by the factor $\phi_1(+)$] adjusts so that the integrated tangential flux of the Ith species of ions driven by the electric field virtually balances that driven by Brownian motion, $i.e.$ there is a Maxwell–Boltzmann distribution around the particle for n_1^I, as well as across the double layer. The tangential electric field also adjusts so that there is virtually no integrated tangential flux of the Ith species advected by the flow.

At low frequencies, the electrophoretic velocity approaches the real value

$$\frac{\varepsilon_w \zeta E}{\mu}\left(1 - \frac{\alpha\beta\{1 + \gamma[1 + \mathcal{O}(kT/e\zeta)]\}}{(1+\alpha\beta)(1+\gamma)}\right).$$

At moderate potentials this takes the classical value $\varepsilon_w\zeta E/\mu$. At higher potentials, this low-frequency limit of the electrophoretic velocity attains a maximum value $\mathcal{O}[2\varepsilon_w kTE\ln(a\kappa_I)/\mu z^I e]$ at $\alpha = \mathcal{O}(1)$, before dropping to a value $\mathcal{O}(\varepsilon_w kT/\mu e)$ at high α. As explained in the section on fluid flow in the double layer, the $\mathcal{O}(kT/e\zeta)$ term in the expression for $\frac{2}{3}V$ requires knowledge about all the species of ions, not just the Ith species. In the case of $z^1 = -z^2$, it is possible to make the necessary calculations analytically and find that this limiting value of the electrophoretic velocity for very high potentials and low frequencies is $2\ln 2\varepsilon_w kTE/\mu ez$. The drop in the electrophoretic velocity corresponds to the drop in the fluid flow as the tangential electric field adjusts to produce virtually no integrated tangential flux of the Ith species advected by the flow.

As the frequency increases, the real part of the polarization decreases monotonically to its high-frequency limit of -1 while the imaginary parts of the polarization increase to a maximum $\mathcal{O}(1)$ before eventually decreasing like $\sigma^{-1/2}$.

The high-frequency form of the polarization is

$$P \sim -1 + \Sigma^{-1/2}(1-i)\frac{3}{\sqrt{2}}\gamma\sqrt{\left(\frac{i\Sigma}{\lambda^2 a^2}\right)} \quad \text{as } \Sigma \to \infty.$$

Thus the approach to the high-frequency limit is independent of the potential (independent of α). The criterion for the frequency to be large, however, is $\Sigma \geqslant 4(1+\gamma)(1+\alpha\beta)/\alpha$. Thus at moderate potentials (low α) the polarization does not attain its high-frequency form until very high frequencies. Note, however, that

our restriction to moderate frequencies does not permit us to consider frequencies above the limit $\Sigma > a^2 \kappa^2$.

At high frequencies the diffusional length scale λ^{-1} becomes small. Only a small value of $n_1^1(+)$ is therefore needed to provide a diffusional flux of the co-ions in order to balance the $\mathcal{O}(1)$ electrically driven flux. Neutrality outside the double layer then requires that $n_1^2(+)$ should also be small. The rapidly oscillating number of the special species of ions in the double layer must be supplied by the integrated fluxes, and this ensures that the number of these ions

$$\int_{\mathrm{dl}} n_1^2 \, \mathrm{d}r = \tfrac{1}{2} \kappa_I^{-1} [n_\infty^2 (ez^2/kT) \phi_1(+) + n_1^2(+)] \exp(-ez^2 \zeta / 2kT)$$

is small. Hence $\phi_1(+) = -Ea(1+P) \cos\theta \exp(i\sigma t)$ is also small and so $P \sim -1$.

RESULTS FOR AN ELECTROLYTE WITH TWO SPECIES OF CHARGED IONS AND WITH THE CONSTANT CHARGE BOUNDARY CONDITION

The results for the constant charge boundary condition are very similar to those for constant potential, except that $i\sigma \int n_1^2$ is now small and terms in Σ therefore vanish. Solving the system of linear equations we find

$$P = \tfrac{1}{2} - \tfrac{3}{2} \alpha\beta / [1 + \gamma + \alpha\beta(1 + \gamma\delta)]$$

and

$$\tfrac{2}{3} V = \frac{\varepsilon_w \zeta E}{\mu} \left(1 - \frac{\alpha\beta\{1 + \gamma\delta[1 + \mathcal{O}(kT/e\zeta)]\}}{1 + \gamma + \alpha\beta(1 + \gamma\delta)} \right).$$

At low frequencies the polarization takes the form

$$P \sim \frac{1}{2} - \left(\frac{3\alpha\beta}{2(1+\gamma)(1+\alpha\beta)} \right) - i\Sigma \frac{3\alpha^2\beta^2 \gamma(\lambda^2 a^2/i\Sigma)}{4(1+\gamma)^2(1+\alpha\beta)^2} \quad \text{as } \Sigma \to 0.$$

The real part is identical to that for the previous case of constant surface potential. The small imaginary part does, however, show the change in the boundary condition.

As the frequency increases, the real part of the polarization decreases monotonically, while the imaginary part increases to a maximum $\mathcal{O}[\alpha^2/(1+\alpha)^2]$ and then decreases at high frequencies like $\sigma^{-1/2}$.

At high frequencies the polarization takes the form

$$P \sim \frac{1}{2} - \left(\frac{3\alpha\beta}{21+\gamma+\alpha\beta} \right) + \Sigma^{-1/2} \frac{(1-i)3}{\sqrt{2}} \left(\frac{\alpha^2\beta^2 \gamma(i\Sigma/\lambda^2 a^2)^{1/2}}{\gamma + \alpha\beta)^2} \right) \quad \text{as } \Sigma \to \infty.$$

For the constant charge boundary condition, the high-frequency limit is attained when $\Sigma = \mathcal{O}(1)$. The limiting mechanism at high frequencies is quite different from the previous case of constant surface potential because now $\int_{\mathrm{dl}} n_1^I \, \mathrm{d}r \sim 0$. The second and third integrals in the flux balance are both proportional to

$$[ez^2 n_\infty^2 \phi_1(+) + kT n_1^2(+)] \exp(-ez^I \zeta / 2kT)$$

and the balance between these integrals and the outer solution determines P. At high potentials this balance requires that $ez^2 n_\infty^2 \phi_1(+) + kT n_1^2(+)$ is small. But, as in the previous case, $n_1^2(+)$ is small at high frequencies. Thus $\phi_1(+)$ is small and $P \sim -1$.

RELAXATION OF THE SURFACE CHARGE DENSITY

In this section we consider an intermediate boundary condition in which perturbations in the surface densities N_1^i of the i species ($i = 1, \ldots, I$, and, additionally, $i = 0$ for charges moving within the particle) are induced by perturbations in the surface potential $\phi_1(r = a)$ according to a first-order kinetic equation

$$\tau^i \dot{N}_1^i + N_1^i + \chi^i \phi_1(r = a) = 0$$

where τ^i is the reaction time constant and χ^i is the surface capacity for the perturbations in surface charge. With the assumed time dependence of the perturbations, the kinetic equation gives

$$N_1^i = -\chi^i \phi_1(r = a)/(1 + i\sigma\tau^i).$$

Before employing any of the earlier results for the structure of the double layer, we must observe that they are based on the distribution within the double layer

$$n_1^I = \exp(-ez^I\phi_0/kT)\{n_1^I(+) - n_\infty^I(ez^I/kT)[\phi_1 - \phi_1(+)]\}.$$

This distribution follows from the leading order approximation of zero net radial flux

$$-\omega^I ez^I(n_1^I \, \partial\phi_0/\partial r + n_\infty^I \, \partial\phi_1/\partial r) - \omega^I kT \frac{\partial n_1^I}{\partial r} = 0.$$

When the surface densities of the ions change, the radial fluxes will not, however, vanish. Estimating the surface ion density N_1^i as $\mathcal{O}[n_1^i\kappa_I^{-1} \exp(-ez^I\zeta/2kT)]$, we see that the surface ion flux $i\sigma N_1^i$ is smaller than $\omega^I kT \, \partial n_1^i/\partial r = \mathcal{O}[\omega^I kT n_1^I \kappa_1 \exp(-ez^I\zeta/2kT)]$ by $\mathcal{O}(a\kappa_I)^{-2}$ at moderate frequencies $\sigma = \mathcal{O}(\omega kT/a^2)$. Thus the non-zero surface flux boundary condition does not change the leading order radial flux balance and the results deduced from it.

Modifying the earlier results for the thin double layer at high surface potential, we apply the electrical boundary condition on the surface charge

$$\varepsilon_w \frac{\partial\phi_1}{\partial r}\bigg|_a = -\sum_0^I ez^i N_1^i$$

to find

$$B_2 = \cos\theta \exp(i\sigma t) z^I \kappa_I^{-1} \exp(ez^I\zeta/2kT)\left\{\tfrac{1}{2}\left(\frac{x}{1+x}\right)\left(\frac{eEa(1+P)}{kT}\right)\right.$$
$$\left. + \tfrac{1}{2}\sum_2^I c_k\left[\frac{x}{1+x} + \frac{1}{1+x}\left(\frac{\lambda_k^2\omega^I kT}{\lambda_k^2\omega^I kT - i\sigma}\right)\right]\right\}$$

and hence

$$\phi_1(r = a) = \frac{\cos\theta \exp(i\sigma t)}{1+x}\left[-Ea(1+P) + \frac{kT}{e}\sum_2^I c_k\left(\frac{i\sigma}{\lambda_k^2\omega^I kT - i\sigma}\right)\right].$$

In these expressions we have introduced

$$x = \sum_0^I x^i \quad \text{with } x^i = \frac{ez^i\chi^i}{\varepsilon_w\kappa_I(1 + i\sigma\tau^i)} \exp(ez^I\zeta/2kT).$$

We can now apply the integrated flux balance, including the surface fluxes, to obtain, for $i \neq 0$ or I

$$-i\sigma N_1^i = \omega^i z^i n_\infty^i$$

$$\times \left[eE(1-2P) + \frac{2kT}{a} \sum_2^I c_k \left(\frac{i\sigma}{\lambda_k^2 \omega^i kT - i\sigma} \right) \left(\frac{1 + \lambda_k a + \frac{1}{2}\lambda_k^2 a^2}{1 + \lambda_k a} \right) \right] \cos \theta \, (i\sigma t)$$

and for the Ith species

$$-i\sigma N_1^I = \omega^I z^I n_\infty^I \left\{ eE(1-2P) + \frac{2kT}{a} \sum_2^I c_k \left(\frac{i\sigma}{\lambda_k^2 \omega^I kT - i\sigma} \right) \left(\frac{1 + \lambda_k a + \frac{1}{2}\lambda_k^2 a^2}{1 + \lambda_k a} \right) \right.$$

$$-\alpha \left[\frac{i}{2} \left(\frac{x}{1+x} \right) \Sigma + 2\beta \right] \left[Ee(1+P) \right.$$

$$\left. \left. -\frac{kT}{a} \sum_2^I c_k \left(\frac{i\sigma}{\lambda_k^2 \omega^I kT - i\sigma} \right) \right] \right\} \cos \theta \exp(i\sigma t).$$

Solving the case of an electrolyte with just two types of charged ions, we find

$$P = \frac{1}{2} - \frac{3}{2} \frac{\alpha \left[\frac{i}{4} \left(\frac{x^0}{1+x} \right) \Sigma + \beta \right]}{1 + \gamma + \alpha \left[\frac{i}{4} \left(\frac{x^0(1+\gamma\delta) + x^1\delta(1-\gamma)}{1+x} \right) \Sigma + \beta(1+\gamma\delta) \right]}.$$

This expression reduces to the previous result for constant surface potential (with perturbations to the surface charge not provided by ions from the electrolyte) when $x^1, x^2, 1 \ll x^0$, and to the previous result for constant surface charge when $x^0, x^1 \ll 1$. We note that the results for constant surface potential with the perturbations in the surface charge provided by the counter-ions, $i.e.$ $x^0, x^1 \ll 1 \ll x^2$, can not be distinguished from the results for constant surface charge, $i.e.$ $x^0, x^1, x^2 \ll 1$, within the asymptotics for thin double layers at high potentials.

We might similarly relate surface dissociation or adsorption to the number density of ions in the solution adjacent to the surface. O'Brien[11] studied this at low surface potentials and found no effect on the dielectric response of the suspension. At higher potentials we observe that the response is, in general, modified.

DIELECTRIC RESPONSE

DeLacey and White[10] show that the mean current $\langle i \rangle$ in a suspension is related to the mean electric field $\langle E \rangle$ by

$$\langle i \rangle = \left(\sum_i \omega^i n_\infty^i e^2 z^{i2} + i\sigma\varepsilon_w \right) (1 - 3cP) \langle E \rangle$$

where c is the (small) volume density of spheres in the suspension. The out-of-phase contribution to the current is interpreted as a permittivity ε^*, and thus

$$\varepsilon^*/\varepsilon_w = 1 - 3c \left(P_{\text{real}} + \sum_i \omega^i n_\infty^i e^2 z^{i2} P_{\text{imag}} / \sigma\varepsilon_w \right)$$

$$= 1 - 3c \left(P_{\text{real}} + \frac{\bar{\omega}}{\omega^I} \frac{a^2\kappa^2}{\Sigma} P_{\text{imag}} \right)$$

where $P = P_{real} + iP_{imag}$ and $\bar{\omega}$ is a mean mobility $\bar{\omega} \sum n_\infty^i z^{i2} = \sum \omega^i n_\infty^i z^{i2}$. The large term in $(a\kappa)^2$ is due to the high conductivity of the suspension. The presence of the particles, and consequent complex P, changes the phase of the current. This shows up as a change in the permittivity, which can be large at low frequencies even if c is small.

The experimental results of Ballario et al.[2] are generally similar to those of Schwan et al.,[1] but are harder to discuss in detail as $a\kappa$ was at most 4. Chew and Sen[7] considered one particular experiment of Schwan et al. and it is convenient to use this as an illustrative example. Schwan studied a suspension of polystyrene spheres in a solution of KCl and measured a low-frequency relative permittivity of 2.4×10^3. The sphere had radius 0.94×10^{-7} m, and we can estimate $a\kappa = 60$ from the conductivity of the suspension. We take $\gamma = 1$ and $\beta = 1.5$. Note that the volume fraction $c = 0.3$ is far from dilute.

At constant surface charge density

$$\varepsilon^*/\varepsilon_w \sim \frac{c(a\kappa)^2}{(a\kappa_I)^2} \left(\frac{9\beta^2\gamma \exp(-ez^I\zeta/kT)}{4(1+\gamma)^2(1+\alpha\beta)^2} \right) \quad \text{as } \Sigma \to 0. \tag{110}$$

100 mV corresponds to $e\zeta/kT = 4$, $\exp(e\zeta/kT) = 55$ and at $a\kappa = 50$ we predict $\varepsilon^*/\varepsilon_0 = 3.3 \times 10^3 c$, which is a factor 2 smaller than the exact results of DeLacey and White[10] (their fig. 2). Electroviscous calculations[13] have similarly shown that thin double-layer analyses are accurate only at very high values of $a\kappa$. ε^* increases with $a\kappa$, as found by DeLacey and White. However, ε^* approaches a limit independent of $a\kappa$ when α becomes small. We require $e\zeta/kT = 3$ to agree with Schwan's experiment. The surface charge density

$$\sigma = -\varepsilon_w \frac{d\phi_0}{dr}\bigg|_{r=a} = \frac{4en_\infty \sinh(e\zeta/2kT)}{\kappa} \quad \text{for a } 1-1 \text{ electrolyte}$$

$$\sim \frac{2en_\infty}{\kappa} \left(\frac{e\zeta}{kT} \right) \quad \zeta \text{ small}$$

$$\sim \frac{e\zeta}{kT} \times 10^{-2} \text{ C m}^{-2} \quad \text{for Schwan's experiment}$$

is therefore much larger than the value 4×10^{-3} C m^{-2} determined by Ballario et al.

At constant potential

$$\varepsilon^*/\varepsilon_w \sim \frac{9c(a\kappa)^2 \exp(-ez^I\zeta/2kT)}{8a\kappa_I} \left(\frac{1+\gamma+2\beta^2\gamma}{(1+\gamma)^2(1+\alpha\beta)^2} \right) \quad \text{as } \Sigma \to 0.$$

This is much larger than for the case of constant surface charge and can be large even in $\exp(-ez^I\zeta/2kT)$ is $\mathcal{O}(1)$. Our theory is not valid for such low potentials, though the case of a symmetric electrolyte could of course be treated analytically for arbitrary ζ. We now require $e\zeta/kT = 0.8$ to agree with Schwan's experiment. This value of ζ is indeed too small for our final result to be valid, but the surface charge density will clearly now be closer to that reported by Ballario.

Note that ε^* is proportional to a (when α is small), as found experimentally by Schwan. However, we also predict $\varepsilon^* \propto \kappa$. Schwan et al. found a slight decrease in ε^* with κ (see their fig. 10), while Ballario et al. found a slight increase. An explanation would require knowledge of how ζ varies with κ.

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