

# The primary electroviscous effect in a suspension of spheres with thin double layers

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We study the primary electroviscous effect in a suspension of spheres when the double layer thickness  $\kappa^{-1}$  is small compared with the particle radius  $a$ . The case of a 1–1 symmetric electrolyte is examined using the methods of Dukhin & coworkers (1974), whilst the asymmetric electrolyte is studied along lines similar to those of O'Brien (1983). Sherwood's (1980) asymptotic results for high surface potentials and high Hartmann numbers are extended and complemented.

## 1. Introduction

A charged particle suspended in an electrolyte attracts a cloud of counter ions. Motion of the surrounding fluid distorts this cloud, and the resulting stress in a suspension of such particles differs from that in a suspension of uncharged particles. This 'primary electroviscous effect' has been studied by Booth (1950), Russel (1978) and Lever (1979) for small potentials  $e\zeta \ll kT$ , where  $\zeta$  is the electric potential at the surface of the particle,  $e$  is the electronic charge and  $kT$  the Boltzmann temperature. They also assumed that the fluid motion around the sphere was changed only slightly by the presence of the charge cloud, i.e. that the electric Hartmann number  $H = \zeta^2 \epsilon / \omega k T \mu_0$  is small, where  $\epsilon$  and  $\mu_0$  are the dielectric constant and viscosity of the suspending fluid (which we shall take to be water), and  $\omega$  is a typical ionic mobility.

Sherwood (1980) removed both these restrictions for charged spheres in a 1–1 electrolyte and obtained numerical and some asymptotic results, while Watterson & White (1981) independently studied the case of high potentials in more general electrolytes. Here we restrict ourselves to a charge cloud that is thin compared with the radius  $a$  of the sphere, and obtain analytic results by a boundary-layer method similar to that of Dukhin and coworkers (reviewed by Dukhin & Derjaguin (1974) and O'Brien (1983)).

We first review in §2 the governing equations and the one-dimensional equilibrium charge cloud on a flat boundary. The local forms of the potential and ion densities inside the deformed charge cloud are then found in §3 in terms of some unknown constants  $n_i^*$  and  $\phi_1^*$  which occur in the quadrupole fields outside the thin charge cloud. After calculating in §4 the fluid motion inside the charge cloud, we derive in §5 linear equations for these unknown constants by balancing the ion fluxes integrated across the charge cloud. These linear relations are examined in §§6–8 in the special cases of low Hartmann number, low potential and high potential respectively.

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## 2. The equilibrium charge cloud

We assume that the suspending electrolyte contains  $I$  species of ion, each with number density  $n^i$  and valence  $z^i$ . The charge density  $\rho$  is therefore

$$\rho = \sum_i n^i z^i e.$$

The electric potential  $\phi$  satisfies Poisson's equation

$$\nabla^2 \phi = -\frac{\rho}{\epsilon},$$

where  $\phi = \zeta$  at the particle surface  $r = a$ , and  $\phi \rightarrow 0$  far from the particle. Thus we are identifying the particle surface as the slipping plane, at which fluid motion occurs, and neglecting any internal structure of the Stern layer, etc. The ions move under the influence of electric and thermodynamic forces with velocity

$$\mathbf{v}^i = \mathbf{u} + \omega^i (-ez^i \nabla \phi - kT \nabla \log n^i),$$

where  $\mathbf{u}$  is the fluid velocity and  $\omega^i$  the mobility of the  $i$ th species of ion. We assume that the ions are not taking part in reactions. They therefore satisfy the conservation equation

$$\frac{\partial n^i}{\partial t} + \nabla \cdot (n^i \mathbf{v}^i) = 0.$$

When  $\mathbf{u} = 0$  the charge cloud is in thermal equilibrium (denoted by a subscript 0). The ionic number density  $n_0^i$  is given by the Boltzmann distribution

$$n_0^i = n_\infty^i \exp\left(\frac{-ez^i \phi_0}{kT}\right),$$

where

$$\sum_{i=1}^I n_\infty^i z^i e = 0$$

for electrical neutrality of the solution away from any charged particles. Inserting this number density into Poisson's equation gives the Poisson-Boltzmann equation

$$\nabla^2 \phi_0 = -e\epsilon^{-1} \sum_{i=1}^I z^i n_\infty^i \exp\left(\frac{-ez^i \phi_0}{kT}\right).$$

Restricting ourselves to the one-dimensional case of a plane double layer, we can integrate this to obtain

$$\frac{1}{2}\epsilon \left(\frac{d\phi_0}{dr}\right)^2 = kT \sum_i n_\infty^i \left(\exp\left(\frac{-ez^i \phi_0}{kT}\right) - 1\right).$$

The thickness of the double layer is measured by the Debye length

$$\kappa^{-1} = \left(\frac{\epsilon kT}{\sum_i e^2 z^{i2} n_\infty^i}\right)^{\frac{1}{2}},$$

and we shall assume throughout that this is small compared with the particle radius  $a$ . The one-dimensional Poisson-Boltzmann equation can be solved analytically for a symmetric electrolyte. When  $z_1 = -z_2 = 1$  the potential is given by

$$\exp\frac{e\phi_0}{2kT} = \frac{A + e^{-\eta}}{A - e^{-\eta}},$$

where  $\eta = (r - a)\kappa$  is distance from the charged surface, non-dimensionalized by  $\kappa^{-1}$ .  $A$  is chosen to satisfy the boundary condition  $\phi = \zeta$  on  $\eta = 0$ :

$$A = \frac{e^h + 1}{e^h - 1},$$

where

$$h = \frac{e\zeta}{2kT}.$$

There are similar results for symmetric electrolytes and arbitrary  $z$ , but no analytic solution is available for the general asymmetric electrolyte. In this case, when the potential is small (as at the outer edge of the charge cloud, or if  $e\zeta \ll kT$ ) we may linearize the Poisson-Boltzmann equation and obtain

$$\phi_0 \propto e^{-\eta}.$$

At high surface potentials the counter-ion with the highest valency, say  $z^I$ , will be more dense than any other ion close to the surface, and thus

$$\frac{1}{2}\epsilon \left(\frac{d\phi_0}{dr}\right)^2 \sim kTn_\infty^I \exp\left(\frac{-ez^I\phi_0}{kT}\right).$$

Integrating

$$\phi_0 \sim \frac{2kT}{ez^I} \log\left(\exp\left(\frac{ez^I\zeta}{2kT}\right) + \kappa_I(r - a)\right),$$

where  $\kappa_I^{-1}$  is a Debye length based on the  $I$ th species

$$\kappa_I^2 = \frac{e^2 z^{I2} n_\infty^I}{2\epsilon kT}.$$

This holds only at high potentials, and only in the inner part of the double layer where

$$r - a = O\left(\kappa_I^{-1} \exp\left(\frac{ez^I\zeta}{2kT}\right)\right).$$

Note that  $z^I\zeta < 0$ .

### 3. The deformed charge cloud

In steady state the number densities of the ions in the deformed cloud satisfy the conservation equation

$$\nabla \cdot [n^i \mathbf{u} - \omega^i (ez^i n^i \nabla \phi + kT \nabla n^i)] = 0.$$

We follow Booth (1950) and assume that the cloud is only slightly deformed from equilibrium, i.e. that the Péclet number  $P$ , measuring the ratio of convection to Brownian diffusion of the ions, is small:

$$P = \frac{U}{\omega kT \kappa} \ll 1.$$

We can therefore expand the number densities and potential as

$$\begin{aligned} n^i &= n_0^i + n_1^i + \dots, \\ \phi &= \phi_0 + \phi_1 + \dots, \end{aligned}$$

where  $n_1^i, \phi_1$  are  $O(P)$ . The perturbations satisfy

$$\begin{aligned} \omega^i \nabla \cdot (ez^i (n_1^i \nabla \phi_0 + n_0^i \nabla \phi_1) + kT \nabla n_1^i) &= \mathbf{u} \cdot \nabla n_0^i, \\ \epsilon \nabla^2 \phi_1 &= -\sum_i ez^i n_1^i, \end{aligned}$$

where we have assumed an incompressible fluid  $\nabla \cdot \mathbf{u} = 0$ . Vorticity merely rotates the particle together with its surrounding charge cloud. We therefore assume that the imposed fluid motion takes the form  $\mathbf{u} = \mathbf{E} \cdot \mathbf{x}$  and look for perturbations in the form of quadrupoles. Outside the double layer

$$\phi_0 = 0, \quad n_0^i = n_\infty^i,$$

and hence

$$n_1^i = n_i^* \mathbf{x} \cdot \mathbf{E} \cdot \mathbf{x} \left(\frac{a}{r}\right)^5, \quad \phi_1 = \phi_1^* \mathbf{x} \cdot \mathbf{E} \cdot \mathbf{x} \left(\frac{a}{r}\right)^5,$$

where

$$\sum_i z^i n_i^* = 0.$$

Inside the double layer the perturbed ion density  $n_1^i$  is given, at leading order, by the radial flux balance

$$ez^i \left( n_1^i \frac{\partial \phi_0}{\partial r} + n_0^i \frac{\partial \phi_1}{\partial r} \right) + kT \frac{\partial n_1^i}{\partial r} = 0,$$

where we have applied the boundary condition that there should be zero flux of ions into the particle surface. Thus we are neglecting any structure or relaxation of the Stern layer. Fluid motion has been assumed negligible, which is justified as normal velocities will be  $O(a\kappa)^{-1}$  smaller than any tangential velocities. We can integrate the flux balance to yield, within the double layer,

$$n_1^i = \exp\left(\frac{-ez^i \phi_0}{kT}\right) \left[ n_1^i(+)-n_\infty^i(\phi_1-\phi_1(+)) \frac{ez^i}{kT} \right],$$

where  $n_1^i(+)$  and  $\phi_1(+)$  are values just outside the double layer:

$$n_1^i(+)=n_i^* \mathbf{x} \cdot \mathbf{E} \cdot \mathbf{x}, \quad \phi_1(+)=\phi_1^* \mathbf{x} \cdot \mathbf{E} \cdot \mathbf{x}.$$

This merely represents a Boltzmann distribution

$$n_0^i+n_1^i \propto \exp\left[\frac{-ez^i(\phi_0+\phi_1)}{kT}\right]$$

after ignoring terms  $O(P^2)$ . The perturbed potential  $\phi_1$  satisfies Poisson's equation

$$\epsilon \frac{\partial^2 \phi_1}{\partial r^2} = -\sum_i ez^i n_1^i(+)\exp\left(\frac{-ez^i \phi_0}{kT}\right) + \sum_i (\phi_1-\phi_1(+)) \exp\left(\frac{-ez^i \phi_0}{kT}\right) \frac{e^2 z^{i2} n_\infty^i}{kT},$$

with solution

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

where

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

$B_2$  is a constant of integration which depends on the boundary condition applied at the surface (e.g. constant charge, constant potential or some more complicated relaxation condition). However,  $B_2$  only enters the analysis at  $O(P^2)$  and need not be specified here. In the case of a 1-1 electrolyte

$$n_1^i(+)=n_1(+), \quad n_\infty^i=n_\infty, \quad n_i^*=n_1^* \text{ say, } \quad i=1, 2,$$

$$f = B_2 + \frac{1}{2} \frac{(r-a)n_1(+)}{n_\infty},$$

whilst for a general electrolyte at high potential

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

in the inner part of the double layer.

#### 4. Motion of fluid within the charge cloud

We assume the particle to be sufficiently small for the Stokes equations to hold:

$$\nabla p = \mu_0 \nabla^2 \mathbf{u} - \rho \nabla \phi,$$

where  $p$  is the pressure and  $\rho \nabla \phi$  is the electric force acting on the fluid. At leading order within the thin charge cloud there is no motion perpendicular to the particle surface and we obtain the perturbed pressure balance

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

which integrates to give

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

The tangential component of the Stokes equations becomes

$$\begin{aligned} \mu_0 \frac{\partial^2 \mathbf{u}_{\text{tan}}}{\partial r^2} &= (\nabla p)_{\text{tan}} + \rho_0 (\nabla \phi_1)_{\text{tan}} \\ &= 2(\mathbf{E} \cdot \mathbf{x} - \mathbf{x}\mathbf{x} \cdot \mathbf{E} \cdot \mathbf{x} a^{-2}) \sum_i \left[ kT n_i^* \left( \exp\left(\frac{-ez^i \phi_0}{kT}\right) - 1 \right) + ez^i n_\infty^I \phi_1^* \exp\left(\frac{-ez^i \phi_0}{kT}\right) \right]. \end{aligned}$$

The second term integrates to give a contribution to  $\mathbf{u}_{\text{tan}}$  of

$$2\left(\mathbf{E} \cdot \mathbf{x} - \frac{\mathbf{x}\mathbf{x} \cdot \mathbf{E} \cdot \mathbf{x}}{a^2}\right) \phi_1^* (\zeta - \phi_0(r)) \mu_0^{-1} e.$$

For a 1-1 electrolyte the first term becomes

$$kT n_1^* (e^{e\phi_0/kT} + e^{-e\phi_0/kT} - 2),$$

which integrates to yield a contribution

$$-8\left(\mathbf{E} \cdot \mathbf{x} - \frac{\mathbf{x}\mathbf{x} \cdot \mathbf{E} \cdot \mathbf{x}}{a^2}\right) \mu_0^{-1} \kappa^{-2} n_1^* kT \left( \ln \frac{A - e^{-\eta}}{A - 1} + \ln \frac{A + e^{-\eta}}{A + 1} \right).$$

More generally we cannot perform this integration, but at high potentials, considering only the dominant  $I$  ions in the inner part of the double layer, we obtain contributions

$$\sim 2\left(\mathbf{E} \cdot \mathbf{x} - \frac{\mathbf{x}\mathbf{x} \cdot \mathbf{E} \cdot \mathbf{x}}{a^2}\right) \mu_0^{-1} (\zeta - \phi_0(r)) \left( \phi_1^* + \frac{kT n_I^*}{ez^I n_\infty^I} \right) e.$$

Beyond the charge cloud the fluid velocity takes the form

$$\mathbf{u} = \mathbf{E} \cdot \mathbf{x} \left( 1 + 2R \left( \frac{a}{r} \right)^5 \right) + \mathbf{x}\mathbf{x} \cdot \mathbf{E} \cdot \mathbf{x} r^{-2} \left( S \left( \frac{a}{r} \right)^3 - 5R \left( \frac{a}{r} \right)^5 \right).$$

We match this with the velocity in the double layer, allowing a small slip but

negligible  $O(a\kappa)^{-1}$  normal velocity at the sphere surface, giving, within the double layer,

$$\mathbf{u}_{\text{tan}} = \left( \mathbf{E} \cdot \mathbf{x} - \frac{\mathbf{x}\mathbf{x} \cdot \mathbf{E} \cdot \mathbf{x}}{a^2} \right) \left( v_s + \frac{5(r-a)}{a} \right),$$

where  $v_s = 2\mu_0^{-1}\phi_1^*\epsilon(\zeta - \phi_0(r)) - 8\mu_0^{-1}\kappa^{-2}n_1^*kT \left( \ln \frac{A - e^{-\eta}}{A-1} + \ln \frac{A + e^{-\eta}}{A+1} \right)$   
for a 1-1 electrolyte,

$$\sim 2\mu_0^{-1}(\zeta - \phi_0(r)) \left( \phi_1^* + \frac{kTn_1^*}{ezI n_\infty^t} \right) \epsilon$$

for a general electrolyte at high potential.

Matching also gives  $R = \frac{1}{2}(v_s^\infty - 1), \quad S = -\frac{5}{2} + \frac{3}{2}v_s^\infty,$

where  $v_s \rightarrow v_s^\infty$  as  $\eta \rightarrow \infty$ .

Now  $S$  is the stresslet term (Batchelor 1970), and so the viscosity of a dilute suspension of charged spheres with volume fraction  $\Phi$  is

$$\mu = \mu_0(1 - S\Phi) = \mu_0(1 + \Phi(\frac{5}{2} - \frac{3}{2}v_s^\infty)).$$

### 5. The flux balance in the deformed double layer

The constants  $n_i^*$  and  $\phi_1^*$  must now be determined. Integrating the equations for the perturbed ion number densities through the double layer, we obtain the integrated flux equation

$$\int_{\text{dl}} \nabla \cdot \mathbf{u} n_0^i \, dr - \int_{\text{dl}} \nabla_t \cdot \omega^t (ez^t n_0^i \nabla_t \phi_1 + kT \nabla_t n_1^i) \, dr = \omega^t \left( ez^t n_\infty^i \frac{\partial \phi_1}{\partial r} \Big|_{\text{dl}+} + kT \frac{\partial n_1^i}{\partial r} \Big|_{\text{dl}+} \right),$$

where  $\text{dl}$  stands for the double layer,  $\text{dl}+$  for just outside the double layer and  $\nabla_t$  is the tangential differential operator. To obtain the above flux balance we have used the results  $\nabla_t \phi_0 = 0$  everywhere,  $\partial \phi_0 / \partial r = n_0^i - n_\infty^i = 0$  outside the double layer, and we have applied the zero flux boundary condition on  $r = a$ .

The first term in the flux balance represents the convection of ions. Since  $\nabla \cdot \mathbf{u} = 0$  and  $n_0^i = n_\infty^i$  outside the double layer,

$$\int_{\text{dl}} \nabla \cdot \mathbf{u} n_0^i \, dr = \nabla_t \cdot \int_{\text{dl}} \mathbf{u}_{\text{tan}} (n_0^i - n_\infty^i) \, dr.$$

For a 1-1 electrolyte we can perform the integrals exactly. We assume that the particle is charged positively and obtain, for the negative counter-ions,

$$\begin{aligned} -6\mathbf{x} \cdot \mathbf{E} \cdot \mathbf{x} n_\infty a^{-2} \kappa^{-1} & \left( \frac{10}{a\kappa} \log \frac{A}{A-1} - 2\phi_1^* \frac{kT\epsilon}{\mu_0 e} \left( \frac{\zeta e}{kT} - 2e^h + 2 \right) \right. \\ & \left. - 8n_1^* \frac{kT}{\mu_0 \kappa^2} \left( e^h - 1 - 3 \log \frac{A}{A-1} - \log \frac{A}{A+1} \right) \right), \end{aligned}$$

and for the positive ions

$$\begin{aligned} -6\mathbf{x} \cdot \mathbf{E} \cdot \mathbf{x} n_\infty a^{-2} \kappa^{-1} & \left( \frac{10}{a\kappa} \log \frac{A}{A+1} - 2\phi_1^* \frac{kT\epsilon}{\mu_0 e} \left( \frac{\zeta e}{kT} + 2e^{-h} - 2 \right) \right. \\ & \left. - 8n_1^* \frac{kT}{\mu_0 \kappa^2} \left( e^{-h} - 1 - 3 \log \frac{A}{A+1} - \log \frac{A}{A-1} \right) \right). \end{aligned}$$

For a general electrolyte at high potentials we can evaluate the integral for the dominant  $I$  counter-ions, obtaining

$$\mathbf{x} \cdot \mathbf{E} \cdot \mathbf{x} \left[ \frac{15\epsilon\zeta}{a^3 ez^I} + \frac{12kT\epsilon}{\mu_0 a^2 ez^I \kappa_I} \left( \phi_1^* n_\infty^I + \frac{kTn_I^*}{ez^I} \right) e^{-ez^I \zeta / 2kT} \right].$$

The corresponding integral for other ions cannot, however, be evaluated, because it is not necessarily dominated by the innermost part of the double layer where  $\phi_0$  is known.

Because the co-ions are excluded from the double layer, their contribution to the next integral, which represents motion of the ions under electric forces and diffusion, is  $O(a\kappa)^{-1}$  small and can be neglected. At high potentials, though, the large number density of the counter-ions compensates for the thinness of the double layer, and we find for the negative ions of a 1-1 electrolyte

$$\nabla_t \cdot \omega^- \int_{dl} (-en_0^- \nabla_t \phi_1 + kT \nabla n_1^-) dr = -12\mathbf{x} \cdot \mathbf{E} \cdot \mathbf{x} \omega^- a^{-2} \kappa^{-1} (kTn_1^* - n_\infty \phi_1^* e) (e^h - 1),$$

whilst for a general electrolyte at high potentials the flux of the important  $I$ th species is

$$-6\mathbf{x} \cdot \mathbf{E} \cdot \mathbf{x} \omega^I a^{-2} \kappa_I^{-1} (kTn_I^* + n_\infty^I \phi_1^* ez^I) e^{-ez^I \zeta / 2kT}.$$

The final terms of the integral flux equation represent the motion of ions due to thermal diffusion and electric forces into the outer, quadrupole region of the deformed charge cloud, and are

$$-3\mathbf{x} \cdot \mathbf{E} \cdot \mathbf{x} \omega^I a^{-1} (ez^I n_\infty^I \phi_1^* + kTn_I^*).$$

We can now substitute these fluxes into the integral flux equation. Looking first at the exact case of a 1-1 electrolyte, the negative ions give

$$\begin{aligned} & \frac{-6n_\infty}{a^2 \kappa} \left( \frac{10}{a\kappa} \log \frac{A}{A-1} - 4\phi_1^* \frac{kT\epsilon}{\mu_0 e} (h - e^h + 1) \right. \\ & \left. - 8n_1^* \frac{kT}{\mu_0 \kappa^2} \left( e^h - 1 - 3 \log \frac{A}{A-1} - \log \frac{A}{A+1} \right) \right) + \frac{12\omega^-}{a^2 \kappa} (kTn_1^* - en_\infty \phi_1^*) (e^h - 1) \\ & = -3(kTn_1^* - en_\infty \phi_1^*) \frac{\omega^-}{a}. \end{aligned}$$

The flux balance for the positive ions is

$$\begin{aligned} & \frac{-6n_\infty}{a^2 \kappa} \left( \frac{10}{a\kappa} \log \frac{A}{A+1} - 4\phi_1^* \frac{kT\epsilon}{\mu_0 e} (h + e^{-h} - 1) \right. \\ & \left. - 8n_1^* \frac{kT}{\mu_0 \kappa^2} \left( e^{-h} - 1 - 3 \log \frac{A}{A+1} - \log \frac{A}{A-1} \right) \right) = -3(kTn_1^* - en_\infty \phi_1^*) \frac{\omega^+}{a}. \end{aligned}$$

Similarly, the flux balance for the  $I$ th ions in the general electrolyte at high potentials is

$$\begin{aligned} & \frac{15\epsilon\zeta}{a^3 ez^I} + \frac{12kT\epsilon}{\mu_0 a^2 \kappa_I ez^I} \left( \phi_1^* n_\infty^I + \frac{kTn_I^*}{ez^I} \right) \exp \left( \frac{-ez^I \zeta}{2kT} \right) \\ & + \frac{6\omega^I ez^I}{a^2 \kappa_I} \left( \phi_1^* n_\infty^I + \frac{kTn_I^*}{ez^I} \right) \exp \left( \frac{-ez^I \zeta}{2kT} \right) = -3\omega^I \left( n_\infty^I \phi_1^* + \frac{kTn_I^*}{ez^I} \right) \frac{ez^I}{a} \end{aligned}$$

or

$$\left( n_\infty^I \phi_1^* + \frac{kTn_I^*}{ez^I} \right) \left( \left( \frac{6\omega^I ez^I}{a^2 \kappa_I} + \frac{12kT\epsilon}{\mu_0 a^2 \kappa_I ez^I} \right) e^{-ez^I \zeta / 2kT} + 3\omega^I ez^I a^{-1} \right) = -\frac{15\epsilon\zeta}{a^3 ez^I}.$$

It is easiest to study these equations for  $\phi_1^*$  and  $n_1^*$  by examining first the 1-1 electrolyte in two limiting cases, corresponding to low Hartmann numbers with arbitrary potentials, and to arbitrary Hartmann numbers at small potentials. We then consider the general electrolyte at high potentials.

## 6. Low Hartmann numbers and arbitrary potentials

If

$$\frac{\phi_1^* k T \epsilon a \kappa (e^h - 1 - h)}{\mu_0 e} \quad \text{and} \quad \frac{n_1^* k T a (e^h - 1 - h)}{\phi_0 \kappa}$$

are small, then  $v_s$  is small compared with the unperturbed motion of the fluid. We can neglect the convection fluxes due to the perturbed flow, and the governing equations become, for a 1-1 electrolyte,

$$\frac{20n_\infty}{a^2 \kappa^2} \log \frac{A}{A-1} = \omega^- (k T n_1^* - e n_\infty \phi_1^*) \left( 1 + \frac{4(e^h - 1)}{a \kappa} \right),$$

$$\frac{20n_\infty}{a^2 \kappa^2} \log \frac{A}{A+1} = \omega^+ (k T n_1^* + e n_\infty \phi_1^*).$$

But

$$\begin{aligned} v_s^\infty &= \mu_0^{-1} \left( 2\phi_1^* \zeta e - 8\kappa^{-2} n_1^* k T \left( \log \frac{A}{A-1} + \log \frac{A}{A+1} \right) \right) \\ &= \frac{-8}{\mu_0 \kappa^2} \left( (k T n_1^* - e n_\infty \phi_1^*) \log \frac{A}{A-1} + (k T n_1^* + e n_\infty \phi_1^*) \log \frac{A}{A+1} \right). \end{aligned}$$

Hence the electrical contribution to the viscosity is

$$-\frac{3}{2} \mu_0 \Phi v_s^\infty = \frac{240 n_\infty \Phi}{a^2 \kappa^4} \left[ \left( \log \frac{A}{A+1} \right)^2 (\omega^+)^{-1} + \left( \log \frac{A}{A-1} \right)^2 \left( 1 + \frac{4(e^h - 1)}{a \kappa} \right)^{-1} (\omega^-)^{-1} \right].$$

Sherwood (1980) expressed this contribution in the form

$$\Phi \frac{(a \kappa)^2 \epsilon}{10 \omega k T} \left( \frac{k T}{e} \right)^2 I(a \kappa, h),$$

where  $I$  was obtained by a numerical solution of the governing equations. Comparing these expressions, we see that, when  $\omega^+ = \omega^- = \omega$  we would expect

$$(a \kappa)^4 I = 1200 \left[ \log^2 \frac{1}{2} (1 + e^{-h}) + \log^2 \frac{1}{2} (1 + e^h) \right] \left( 1 + \frac{4(e^h - 1)}{a \kappa} \right),$$

and in figure 1 we compare the two sides of this expression. When  $a \kappa = 100$  the maximum predicted by this analysis is too high by 10%. At  $a \kappa = 10^3$  the analytic and numerical curves coincide.

At low potentials the tangential motion of the ions in the double layer due to diffusion and electric forces is negligible, and convection of ions in the double layer is balanced by the fluxes into and out of the outer quadrupole cloud. As the potential increases, so the density of counter-ions becomes large. At first the tangential diffusion and electric fluxes remain negligible and convection of the more numerous counter-ions is unchanged in order of magnitude because the ions are confined to the inner part of the double layer where the fluid flow is small. At higher potentials the tangential diffusion and electric fluxes become very large, and in order that the fluxes balance, the tangential driving force  $\propto (k T n_1^* - e n_\infty \phi_1^*)$  becomes small, resulting in



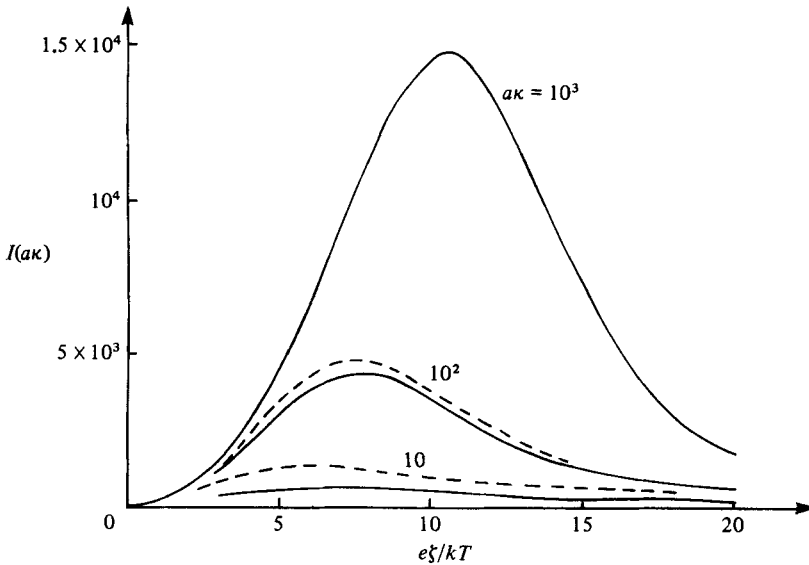


FIGURE 1. Electrical contribution to the intrinsic viscosity as a function of  $\zeta$ , at small Hartmann numbers. Comparison of full numerical results (Sherwood 1980) with analytic results obtained here (shown broken). The curves coincide when  $a\kappa = 10^3$ .

a small contribution of the counter-ions to the electroviscous effect. The co-ions, meanwhile, are present only in the outer part of the double layer, where the potential saturates as  $\zeta \rightarrow \infty$  with far-field form  $4kTe^{-1} \exp(-\eta)$ . We observe that their contribution to the electroviscous effect similarly saturates. At intermediate potentials it is small compared with effects due to the counter-ions, while at very high potentials the counter-ion contribution decays, leaving only that of the co-ions.

Note that

$$\begin{aligned} \phi_1^* &= -10(a\kappa)^{-2} e^{-1} \left( \frac{\log(A/(A-1))}{\omega^-(1+4(e^h-1)/a\kappa)} - \frac{\log(A/(A+1))}{\omega^-} \right) \\ &= \frac{-5\zeta}{(a\kappa)^2 kT} \left( \frac{1}{\omega^-} + \frac{1}{\omega^+} \right) \quad \text{for small } \zeta. \end{aligned}$$

Thus our assumption of small  $\phi_1^*$  and  $n_1^*$  requires

$$H = \frac{\epsilon\zeta^2}{\omega kT\mu_0 a\kappa} \ll 1,$$

with similar restrictions at high potentials.  $H$  is the Hartmann number, measuring the ratio of electric to viscous stresses within the fluid. When  $a\kappa$  is large our assumption  $H \ll 1$  is reasonable. For more general  $a\kappa$  it is not obvious that we can make this restriction. However, Sherwood (1980) showed that only small errors are introduced by making this approximation at typical Hartmann numbers. In §7 we study the effect of the Hartmann number on our analytic results, taking  $\zeta$  small for convenience, and compare with previous numerical results.

### 7. Arbitrary Hartmann numbers at low potentials

When the potential is low the flux balances for a 1-1 electrolyte yield

$$kTn_1^* - en_\infty \phi_1^* = \frac{n_\infty}{\omega^- a\kappa} \left( \frac{10h}{a\kappa} + \frac{4\phi_1^* kTh^2\epsilon}{\mu_0 e} \right),$$

$$kTn_1^* + en_\infty \phi_1^* = \frac{-n_\infty}{\omega^+ a\kappa} \left( \frac{10h}{a\kappa} + \frac{4\phi_1^* kTh^2\epsilon}{\mu_0 e} \right).$$

Hence

$$\phi_1^* = \frac{-5\zeta}{\omega kT(a\kappa)^2(1+H)},$$

$$n_1^* = \frac{5n_\infty h}{(a\kappa)^2 kT(1+H)} \left( \frac{1}{\omega^-} - \frac{1}{\omega^+} \right),$$

where

$$2\omega^{-1} = (\omega^-)^{-1} + (\omega^+)^{-1}.$$

At high Hartmann numbers  $\phi_1^*$  adjusts so that the flux of each type of ion advected by the unperturbed flow is balanced by the flux advected by the flow forced by the restoring electric field. The slip caused by the perturbed flow is

$$v_s^\infty = -10H(a\kappa)^{-1} \left( 1 + \frac{\phi_1^* z a \kappa \epsilon}{5\mu_0} \right),$$

and the electrical contribution to the viscosity is therefore

$$\frac{15\mu_0 \Phi H}{a\kappa(1+H)}.$$

We have assumed that the potential and ion number densities in the double layer are locally in equilibrium, matching with the quadrupole field  $\phi_1^*$ . There will be additional variations within the cloud,  $O(a\kappa)^{-1}$  smaller, which we have neglected. These will not decrease with  $\phi_1^*$ , so there is a risk that they become important when  $\phi_1^*$  is small. Hence the analysis is restricted to  $H \ll a\kappa$ .

In figure 2 we show our analytic result for the intrinsic viscosity  $15H/a\kappa(1+H)$ , together with numerical calculations for  $a\kappa = 500$  (Sherwood 1980). Our analysis does indeed break down at  $H \sim a\kappa$ . At this value the electric stresses are so strong that fluid adjacent to the particle can hardly move, and Sherwood's asymptotic analysis takes over.

### 8. The general electrolyte

In the general case we can only obtain the flux balance for the dominant  $I$ th species of ion when the potential is high:

$$n_\infty^I \phi_1^* + \frac{kTn_I^*}{ez^I} = \frac{-5\epsilon\zeta/a^2 e^2 z^{I^2} \omega^I}{1 + \frac{2}{a\kappa_I} (1 + 2\mathcal{H}) e^{-z^I h}},$$

in which the parameter

$$\mathcal{H} = \frac{ekT}{\mu_0 e^2 z^{I^2} \omega_I}$$

occurs naturally as a Hartmann number based on the ions. If we assume that

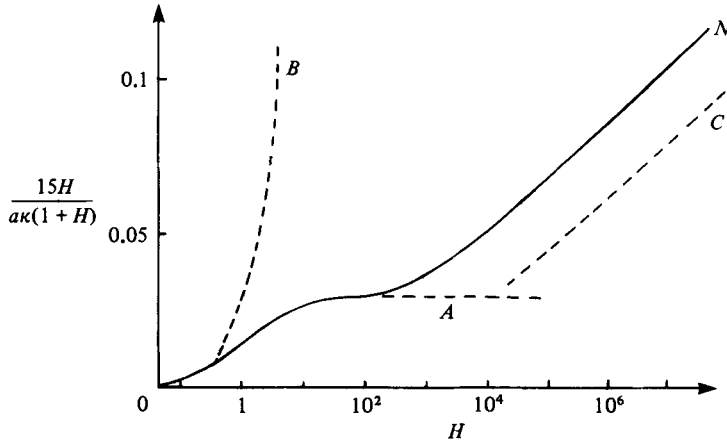


FIGURE 2. Electrical contribution to the intrinsic viscosity, at low potentials, as a function of the Hartmann number  $H$ .  $N$ , full numerical results.  $A$ , analytic results of this paper.  $B$ , Booth's (1950) results for small Hartmann number.  $C$ , Sherwood's asymptotic results for  $H \gg 1$ .  $a\kappa = 500$ .

$\omega_I^{-1} = 4\pi\mu a_I$ , where  $a_I$  is the radius of an ion, and that the potential  $\phi_I$  at the surface of the ion is

$$\phi_I = \frac{z^I e}{4\pi\epsilon a_I},$$

then

$$\mathcal{H} = \frac{z^I e \phi_I}{kT}.$$

The electrical contribution to the viscosity at high potentials is

$$-\frac{3}{2}\mu_0 \Phi v_s^\infty = \frac{30\mu_0 \Phi \mathcal{H} (z^I h)^2 (a\kappa_I)^{-1}}{a\kappa_I + (2 + 4\mathcal{H}) e^{-z^I h}}.$$

The dependence on the Hartmann number  $\mathcal{H}$  is similar to that obtained at low potentials. As a function of the surface potential, the contribution to the viscosity has a maximum at

$$z^I h \sim -\log\left(\frac{a\kappa_I}{2 + 4\mathcal{H}}\right),$$

and the factor  $\mathcal{H}$  causes the maximum to vary (roughly) as  $z_I^{-2}$  when  $a\kappa_I$  is held constant. Similar behaviour, at constant  $a\kappa$ , is observed in the full numerical solutions of Watterson & White (1981). We note finally that at very high potentials our expression tends to zero. We have, however, completely ignored the small contribution of the co-ions, which becomes dominant in this limit.

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