## Electrophoresis of gas bubbles in a rotating fluid

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(Received 17 September 1984 and in revised form 19 July 1985)

The electrophoretic velocity of a gas bubble is difficult to measure, since we must also contend with velocities due to buoyancy. One way to avoid this problem is to spin the electrophoretic cell about a horizontal axis. Centrifugal forces keep the bubble on the centreline of the cell. The price to be paid is the creation of Taylor columns which alter the hydrodynamic drag on the bubble.

Here we modify two analyses by Moore & Saffman (1968, 1969) to include electrical effects. Motion of the body is assumed to be slow and steady, and the Ekman number small. The electrical double-layer thickness is small compared with the thickness of the Ekman layer. It is assumed that the presence of surfactants makes the gas-water interface rigid, and a no-slip boundary condition is applied.

We predict that the electrophoretic velocity U should be proportional to  $eE\psi_0(a\mu)^{-1}(\nu/\Omega)^{\frac{1}{2}}$ , where E is the applied electric field, e the permittivity of the suspending fluid,  $\psi_0$  the  $\zeta$  potential at the surface of the bubble, a the bubble radius,  $\mu$  the fluid viscosity,  $\nu$  the kinematic viscosity and  $\Omega$  the rate of rotation. There is reasonable agreement with some, but not all, published experimental results.

## 1. Introduction

Figure 1 shows an (idealized) electrophoretic cell. Usually we measure the electrophoretic velocities of particles which are small, and which have a density similar to that of the suspending fluid. Sedimentation is therefore not a problem. A large gas bubble, however, will quickly move towards the upper wall of the cell. One way to overcome this is to rotate the entire cell, as is done in the spinning-drop interfacial tensiometer. Experiments are reported by McTaggart (1914), Alty (1924), Whybrew, Kinzer & Gunn (1952), Huddleston (1974), Huddleston & Smith (1975), and McShea & Callaghan (1983). Other techniques have also been adopted – we draw the reader's attention to Collins, Motarjemi & Jameson (1978).

We assume that both the Rossby number  $U/a\Omega$  and the Ekman number  $\vec{E} = \nu/a^2\Omega$ are small, where U is the electrophoretic velocity, a the radius of the bubble,  $\nu$  the kinematic viscosity and  $\Omega$  the angular velocity of the rotating cell. (We reserve the symbol E for the strength of the applied electric field.) Taylor columns will be established in front of, and behind, the bubble. These modify the hydrodynamic forces on the bubble, rendering invalid the usual Smoluchowski analysis for electrophoresis with thin electrical double layers. We therefore modify analyses by Moore & Saffman (1968, 1969) to include electrical effects. Two cases will be considered, corresponding to an electrophoretic cell which is either short or long compared with the length of the Taylor column. Gas bubbles rising through water under buoyancy collect contaminants on their surface, and, at a radius < 0.1 mm, rise with the velocity corresponding to a no-slip boundary condition (Levich 1962). We shall assume that this condition holds throughout our analysis. We shall also assume that surface tension is sufficiently strong to hold the bubble spherical, with radius a.



FIGURE 1. The rotating electrophoretic cell.

 $E \leq 1$  implies that Ekman layers will develop on the surface of the body (see figure 1). Taking  $\nu = 10^{-6}$  m<sup>2</sup> s<sup>-1</sup> and  $\Omega = 100$  s<sup>-1</sup> gives an Ekman-layer thickness  $\lambda^{-1} = (\nu/\Omega)^{\frac{1}{2}} = 10^{-4}$  m compared with a typical value for *a* of  $10^{-4}-10^{-3}$  m. At lower angular velocities, or for small particles, our assumption of thin Ekman layers will become poor.

The charged sphere will be surrounded by an electric charge cloud of counter-ions. The thickness of the cloud is given by the Debye length

$$\kappa^{-1} = \left(\frac{e^2}{ekT}\sum_i z_i^2 n_i\right)^{-\frac{1}{2}}.$$

where  $n_i$  are ionic number densities and  $z_i$  the corresponding valencies.  $\epsilon$  is the permittivity of the suspending fluid,  $\epsilon$  the electronic charge and kT the Boltzmann factor. At an ionic strength of  $10^{-6}$  moles/litre, we obtain  $\kappa^{-1} = 3 \times 10^{-7}$  m for a 1–1 electrolyte, and the Debye length will be smaller still at higher ionic strengths. Thus it is clear that the electrical double layer lies well within the Ekman layer, and may be assumed thin and plane. Thus at low potentials the charge density  $\rho_0$  in the cloud is

$$\rho_0 = -\epsilon \kappa^2 \psi_0 e^{-\kappa z},$$

where z = 0 is the charged surface and  $\psi_0$  is the  $\zeta$  potential at the surface.

## 1.1. Electrical Ekman layers

It is straightforward to modify the standard analysis of an Ekman layer to include electrical stresses. Let (u, v, 0) be velocities in the (x, y, z)-directions, with u = v = 0on the solid surface z = 0, and  $(u, v) \rightarrow (U, 0)$  as  $z \rightarrow \infty$ . The rotation  $\Omega$  is along the z-direction. The electrical force on the fluid  $E\rho_0$  has magnitude  $E\epsilon\kappa^2\psi_0 e^{-\kappa z}$  in the y-direction. If  $\rho$  (without the subscript 0) is the fluid density, and  $\mu = \rho v$  is the fluid viscosity, the equations for steady motion become

$$-2v\Omega = v \frac{\mathrm{d}^2 u}{\mathrm{d}z^2}, \quad 2u\Omega = 2U\Omega + E\epsilon\kappa^2 \psi_0 \mathrm{e}^{-\kappa z} \rho^{-1} + v \frac{\mathrm{d}^2 v}{\mathrm{d}z^2},$$

with solution

$$u - U + iv = -U e^{-\lambda z} (\cos \lambda z - i \sin \lambda z) + \frac{E\epsilon \kappa^2 \psi_0 (1 - \nu i \kappa^2 / 2\Omega)}{2\rho \Omega (1 + \nu^2 \kappa^4 / 4\Omega^2)} (e^{-\kappa z} - e^{\lambda z} (\cos \lambda z - i \sin \lambda z)).$$

Thus

$$\int_0^\infty v\,\mathrm{d}z = \frac{U}{2\lambda} + \frac{E\epsilon\psi_0}{2\mu\lambda},$$

which has been simplified by our assumption  $\kappa \ge \lambda$ . Thus the flux within the Ekman layer consists of the standard hydrodynamic flux, together with an electrical term.

We assume that there is no flux of ions into or out of the surface of the bubble. Since the electrical double layer has a small capacity at low potentials, the imposed electric field is that around a perfect insulator and, in spherical polar coordinates, the potential  $\Phi$  is  $\Phi = F(n + 1n^3n^{-2}) \cos \theta$ 

$$\Phi = -E(r + \frac{1}{2}a^3r^{-2})\cos\theta.$$

Thus the tangential component of the electric field at the bubble surface is

$$E_{\theta} = -\frac{3}{2}E\sin\theta.$$

We follow the notation of Moore & Saffman (1968) and henceforth use cylindrical polar coordinates  $(r, \theta, z)$  with Oz parallel to the axis of rotation and thus to the electric field. We assume that the equation of the particle surface is  $z = \pm f(r)$ ,  $0 \le r \le a$ , where, for our sphere,  $z = a - (a^2 - r^2)^{\frac{1}{2}}$ . The rate of rotation normal to the surface becomes  $\Omega(1 + f'^2)^{-\frac{1}{2}}$ .

Figure 1 shows the geometry to be considered. The multilayer structure of the shear layer between the Taylor column and the outer fluid has been considered by Stewartson (1966) and by Moore & Saffman (1969), who show that there is an inner layer of thickness  $a\tilde{E}^{\frac{1}{3}}$ , and two outer layers of thickness  $a\tilde{E}^{\frac{1}{3}}$  and  $a\tilde{E}^{\frac{3}{2}}$ . In §2 we show that this structure is not modified by the presence of electrical forces. In figure 1 the Taylor column is depicted long compared with the length h of the electrophoretic cell. This is the case considered by Moore & Saffman (1968) and will be considered in §2. For this analysis to hold, we require that h should be large compared with the Ekman-layer thickness. The width of the shear layer (which for the  $\frac{2}{7}$  layer can be shown to be  $O((h/a)^{\frac{4}{7}}a\tilde{E}^{\frac{3}{7}}))$  should also be small compared with a, and these two conditions lead to

$$\lambda^{-1} \ll h \ll aE^{-\frac{1}{2}}.$$

When  $h \ge a\tilde{E}^{-1}$  the Taylor column is damped out by viscosity before it reaches the ends of the cell, and the bubble moves as in an unbounded fluid. This case was studied by (amongst others) Moore & Saffman (1969), and we examine it in §3. While we have thus considered the effect of the end walls of the electrophoretic cell, we shall neglect the presence of the side walls. In a standard cell, the electrical double layers at these walls produce motion of the fluid in the cell, which cannot be ignored. Rotation of the cell will suppress both these fluid velocities and the motion of the bubble: a separate study would be needed to consider these electro-osmotic velocities and will not be attempted here. We note simply that Huddleston (1974) usually performed experiments in a cell made of borosilicate glass, with negatively charged walls. Coating the walls with a cationic silane, trimethoxysilylpropyl trimethyl ammonium chloride, reversed the charge on the walls of the cell and thus reversed the direction of the electro-osmotic flow. The measured electrophoretic velocity of a gas bubble, however, remained unchanged, indicating that the electro-osmotic velocities were negligible.

Finally in §4 we discuss the degree of agreement between theory and published experimental results.