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Electrophoresis of surfactant-free bubbles

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Abstract

In 1996 Kelsall *et al.* reported electrophoretic experiments with oxygen bubbles in dilute solutions of several salts that were remarkably free of surfactants, but the experimental results agree with neither their own theory nor anyone else's known to the present author. This paper assumes a double layer thickness much smaller than the bubble radius, as it was in the experiments. It redevelops the theory on various hypotheses about the precise location of the free surface charge, and both with and without van der Weg's recently-suggested modification to the electrochemical potential. The results suggest that the free surface charge is at or on the gas side of the change in permittivity at a bubble's surface in a surfactant-free liquid, and that the classical theory for the speed of rise of a bubble is not quite correct in an electrolyte solution, but the correction is too small to measure. However, there are still unresolved difficulties with both theory and experiments, which van der Weg's suggestion does not remove. Nor does it improve the fit between theory and Grahame's (1947) experiments on the differential capacitance of a double layer.

Keywords: electrophoresis, bubble, Gouy-Chapman, van der Weg

1. Introduction

Experiments on the rate of rise under gravity or on electrophoresis of gas bubbles in water require extraordinary care if surfactant effects are to be removed. High-purity salts and double-distilled water kept out of contact with laboratory air were found to be insufficient [1] without also purging the apparatus with swarms of electrogenerated bubbles from a pair of Pt electrodes in the cell and sweeping residual surfactants over a weir as those bubbles rose to the surface. Even that was shown to be insufficient by Yurdakul [2, Chapter 6], who improved the cell design by maximising the volume purged, and was able to start with source water of purity comparable to the best water of Brandon *et al.*[1], who had worked in the same laboratory several years earlier. Many other experiments have been done on electrophoresis of gas bubbles in water, but the only ones known to the author in which surface cleanliness was confirmed by showing that bubbles rose under gravity as they would in a pure liquid were by Kelsall *et al.*[2–5]. That test was pioneered in electrophoretic work by Collins *et al.*[6], who found that their own bubbles did not satisfy it, rising under gravity significantly slower than clean-surfaced ones would have, but significantly faster than rigid ones.

If U_{rigid} is the speed of rise under gravity alone expected for a rigid body of the same shape, size and mass as the bubble, U is the actual speed of rise, a is the radius of a sphere with the same volume as the bubble, subscripts ℓ and g indicate liquid and gas, ρ_ℓ and ρ_g are the densities, and γ is the surface tension, then the bubble shape is spherical in the limit of small Weber number $We = 2U^2a\rho_\ell/\gamma$. In an electric field E_∞ , sphericity

also requires that the Maxwell stress (of order $\varepsilon_\ell E_\infty^2$) be much smaller than the surface-tension pressure difference across the surface (of order γ/a). So their ratio, which it seems appropriate to call the “Zeleny number” Ze [7], must obey

$$Ze = \varepsilon_\ell E_\infty^2 a / \gamma \ll 1. \quad (1)$$

If the Reynolds number $Re = 2Ua\rho_\ell/\eta_\ell$ is also small, where η_ℓ is the liquid viscosity, then Stokes's law for a rigid sphere holds for a surface-contaminated spherical bubble:

$$U = U_{rigid} = \frac{2}{9}(\rho_\ell - \rho_g)ga^2/\eta_\ell, \quad (2)$$

where g is the acceleration due to gravity. For a clean-surfaced bubble with $We \ll 1$ and $Re \ll 1$ we have the Rybczyński-Hadamard law giving the speed U_{RH} as

$$U = U_{RH} = \frac{3(\eta_\ell + \eta_g)}{2\eta_\ell + 3\eta_g} U_{rigid}. \quad (3)$$

The electrophoretic mobility is $u_E = U_E/E_\infty$, where U_E is the speed of the bubble relative to the fluid far from it in the motion due to an imposed electric field E_∞ . It is taken to be positive if U_E and E_∞ are in the same direction. Kelsall *et al.* [5] measured the electrophoretic mobilities of bubbles with radii a of 30, 40 and 45 μm in a 10^{-4} M aqueous solution of NaClO_4 at 295 K; the double layers around the bubbles would have been much thinner than their radii.

Booth [8] began the theory of electrophoresis of bubbles and drops with mobile surfaces, ignoring both polarization of the double layer and terms of order ζ^2 where ζ is the potential difference across it. His Eq. (3.13) giving the mobility of a bubble of radius much larger than the double-layer thickness is,

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on conversion to SI units,

$$u_E = \frac{3\varepsilon_\ell \zeta \eta_g}{\eta_\ell (2\eta_\ell + 3\eta_g)}, \quad (4)$$

where ε_ℓ is the liquid permittivity. That mobility disagrees with the experiments [5]: it is independent of both E_∞ and a and is far too small.

Baygents and Saville [9] assumed a zero resultant force, and also assumed that the dimensionless electric field strength \tilde{E}_∞ (β in their notation) obeyed $|\tilde{E}_\infty| \ll 1$, where

$$\tilde{E}_\infty = aeE_\infty/kT; \quad (5)$$

e is the elementary charge, k is Boltzmann's constant, and T is the absolute temperature. They did not make Booth's small- ζ assumption, and they confirmed that in the low- ζ limit their result agreed with (4), but their small- \tilde{E}_∞ theory is of dubious validity for experiments [5] in some of which $|\tilde{E}_\infty|$ was larger than 20.

Kelsall *et al.* [5] themselves gave a third theory, in which the flow field relative to the bubble and outside the double layer on its surface was assumed the same as for a bubble with a free surface moving under an applied force, *i.e.* the superposition of a uniform stream and a Stokeslet (point force flow) at the centre. It was also assumed that the force was that which the imposed electric field E_∞ far from the bubble would exert on the total surface charge on the bubble. That theory gave the electrophoretic mobility as

$$u_E = q_E a / \eta_\ell, \quad (6)$$

where q_E is the free surface charge density, omitting the bound charges which exist at the surface because of the change in permittivity there. A problem with that theory is that the ions in the diffuse double layer are also acted on by the electric field, but that was not taken into account. Another is that it gave $u_E \propto a$. That agrees only partially with Fig. 1 of Kelsall *et al.*, [5] in which the graphs of u_E against a are indeed straight lines, but not through the origin. Another is that it gave u_E independent of E_∞ , but the experimental values increased with E_∞ . Another is that, with the measurements of u_E , it gave a surface electric charge about half what they found by a different method: [5] finding what concentration of an oppositely charged surfactant added to the liquid would reduce the electrophoretic mobility to zero by neutralising the surface charge.

We therefore still need a theory of bubble electrophoresis in the absence of surfactants that is not open to those objections. We also need more tests of van der Weg's [10] recently-suggested modification to the classical theory of electrochemical potential: if z_i is the signed valency of ion i , n_i its number density, and $n_{i\infty}$ the value of n_i outside the double layer, and the parameter $\beta = 1$ in the classical theory [11, 12], but $\beta = 1/\sqrt{2}$ in van der Weg's, then the electrochemical potential μ_i (J/ion) is

$$\mu_i = \mu_{0i} + kT \ln(n_i/n_{i\infty}) + \beta^2 z_i e \phi, \quad (7)$$

where ϕ is the electrical potential. Van der Weg pointed out that his suggestion improves the fit between theoretical and experimental potentials of the hydrogen-calomel cell, and that it

also agrees with the result in classical electrostatics that the work required to assemble a distribution of charges Q_i from infinity is $\frac{1}{2} \sum Q_i \phi_i$, not $\sum Q_i \phi_i$, if ϕ_i is the potential due to the other charges at the position of Q_i .

The purposes of this paper are to rederive the theory of bubble electrophoresis with van der Weg's suggestion in mind and to test it against experimental results on differential capacitance of a double layer [13] and on electrophoretic mobility [5].

2. Electrical theory

In the experiments of Kelsall *et al.* [5], both the Weber and Zeleny numbers were so small that we may take the bubbles to be spherical: We was of order 10^{-8} and Ze was of order 10^{-5} . We assume that the whole configuration is independent of time in the bubble's frame of reference, and use spherical polar coordinates (r, θ) in which the surface, defined as the position of the change in permittivity from ε_ℓ to ε_g , is at $r = a$, and $\theta = 0$ points vertically upwards. The experimental electric fields [5] were vertical far from the bubble, so we may assume symmetry about a vertical axis. The potential $\phi \sim -E_\infty r \cos \theta$ for $r \gg a$, where $E_\infty > 0$ if the field $\mathbf{E} = -\nabla\phi$ is upwards. Let z_i be the charge number of ion i , n_i its number density, and $n_{i\infty}$ the value of n_i outside the double layer. Then the double-layer thickness is of the order of the Debye length λ , where

$$\lambda^{-2} = \kappa^2 = \frac{e^2}{\varepsilon_\ell kT} \sum z_i^2 n_{i\infty}, \quad (8)$$

and the sum is over the species of ions present [11]. In the experiments [5] λ was about 30 nm, and $a \geq 30 \mu\text{m}$, so that $\kappa a \geq 1000$.

For simplicity, we deal with the case of two ionic species with $z_1 = 1$, $z_2 = -1$, which was a good approximation in most of the experiments with nearly neutral pH. We may then put $n_{1\infty} = n_{2\infty} = n_\infty$.

2.1. Non-dimensionalization and subscripts

Symbols bearing a tilde (\sim) indicate a variable or operator made dimensionless by dividing by: a for length, n_∞ for number density, $\Phi = kT/e$ for electrical potential, $\tilde{\Phi}/a$ for electric field, ε_ℓ for permittivity, $\sigma = \varepsilon_\ell \tilde{\Phi}/a$ for surface charge density, σ/a for volume charge density, $F = \varepsilon_\ell \tilde{\Phi}^2$ for force, F/a for surface tension, F/a^2 for stress, η_ℓ for viscosity, $V = F/(\eta_\ell a)$ for velocity, $Va/\Phi = \varepsilon_\ell \tilde{\Phi}/\eta_\ell$ for electrophoretic mobility, and Va^2 for Stokes stream function. In the experiments of Kelsall *et al.* [5], $\tilde{\lambda} < 0.001$, $\Phi = 25.7$ mV, $\sigma = 0.446 \mu\text{C}/\text{m}^2$, $F = 0.458$ pN, $V = 12.9 \mu\text{m}/\text{s}$, $\tilde{\zeta} \approx -0.03$ at neutral pH, and $\tilde{q}_E \approx 30$ if $2a = 80 \mu\text{m}$. Their highest value of $|\tilde{E}_\infty|$ was 12.7 kV/m for a bubble with $2a = 91 \mu\text{m}$ held at rest by the electric field. For that case $|\tilde{E}_\infty| = 22.5$.

It is also convenient to use $s = \sin \theta$, $c = \cos \theta$, and a radial variable y and an operator ∇_y made dimensionless with λ instead of a , because λ is the length scale of variation in the double

layer:

$$y = \beta\kappa(r - a) = \beta\tilde{\kappa}(\tilde{r} - 1), \quad (9)$$

$$\nabla_\lambda = \frac{\lambda}{\beta} \nabla = \frac{\tilde{\lambda}}{\beta} \tilde{\nabla} = \left(\frac{\partial}{\partial y}, \frac{\tilde{\lambda}}{\beta\tilde{r}} \frac{\partial}{\partial \theta} \right), \quad (10)$$

$$\nabla_\lambda^2 = \frac{\lambda^2}{\beta^2} \nabla^2 = \frac{\partial^2}{\partial y^2} + 2 \frac{\tilde{\lambda}}{\beta\tilde{r}} \frac{\partial}{\partial y} + \frac{\tilde{\lambda}^2}{\beta^2 \tilde{r}^2 s} \frac{\partial}{\partial \theta} \left(s \frac{\partial}{\partial \theta} \right). \quad (11)$$

Let subscripts $+$, $-$ indicate the limits as $y \rightarrow 0$ from above (through the liquid) and from below (through the gas). Let subscript q indicate the position $y = y_q$ of q_E (not assumed to be exactly at $y = 0$ where the permittivity changes from ε_g to ε_ℓ). Let y_m, y_M indicate the lesser and greater of $0, y_q$, and let subscripts m, M on other variables indicate the values of those variables at $y = y_m, y = y_M$. As $\kappa a \gg 1$, there is a position $r = b$ in the liquid close to the bubble where $b/a \approx 1$, but well outside the double layer, so $\kappa(b - a) \gg 1$. Let subscript b indicate the position $y_b = \beta\kappa(b - a)$ where $r = b$. Then the dimensionless zeta potential difference across the diffuse double layer in the liquid is $\tilde{\zeta} = \tilde{\phi}_M - \tilde{\phi}_b$, and if the dimensionless potential difference across the surface due to a layer of dipoles there [5, 8] is $\tilde{\chi}$, then $\tilde{\phi}_- - \tilde{\phi}_b = \tilde{\zeta} + \tilde{\chi}$ unless there is a Stern layer. Fig. 1 indicates how the potential varies with position in the three possible cases $y_q > 0, y_q = 0, y_q < 0$. It is drawn for the case $\zeta < 0, \chi < 0$.

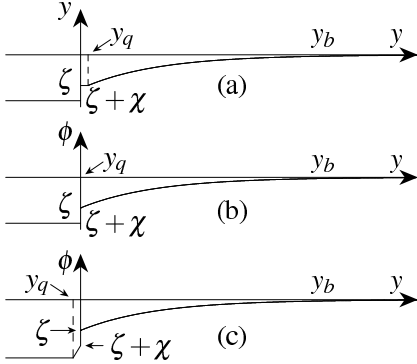


Figure 1: Schematic plots of potential ϕ against y near a surface, ignoring contributions from the imposed field E_∞ , in the three cases (a): $y_M = y_q > 0, y_m = 0$; (b): $y_M = y_m = y_q = 0, y_m = 0, y_q < 0$; (c): $y_M = 0, y_m = y_q < 0$.

2.2. Electric field outside the double layer: first approximation

As the gas is non-conducting and the liquid is an electrolyte, $\nabla^2 \phi = 0$ in both phases except in the double layer. Conduction in the double layer itself is negligible in the absence of surfactants when $\tilde{\lambda} \ll 1$. If ζ and χ are both independent of θ , then the leading terms for the dimensionless potentials $\tilde{\phi}_\ell, \tilde{\phi}_g$ in the liquid and gas outside the double layer, and the field components

$\tilde{E}_r, \tilde{E}_\theta$ outside the double layer but near it, are

$$\tilde{\phi}_\ell = -\tilde{E}_\infty \left(\tilde{r} + \frac{1}{2} \tilde{r}^{-2} \right) c, \quad (12)$$

$$\tilde{\phi}_g = -\frac{3}{2} \tilde{E}_\infty \tilde{r} c + \tilde{\zeta} + \tilde{\chi}, \quad (13)$$

$$\tilde{E}_{r\ell} = \frac{3}{2} \tilde{E}_\infty c, \quad (14)$$

$$\tilde{E}_{r\ell} = 0, \quad (15)$$

$$\tilde{E}_{\theta g} = \tilde{E}_{\theta b} = -\frac{3}{2} \tilde{E}_\infty s. \quad (16)$$

In addition to q_E there must be a bound surface charge density at $\tilde{r} = 1, q_B$ say, because of the discontinuity of permittivity there. The double layer has no net free charge, so Gauss's theorem, (14) and (15) give

$$\tilde{q}_B = \tilde{E}_{r\ell} - \tilde{\varepsilon}_g \tilde{E}_{r\ell} = -\frac{3}{2} \tilde{\varepsilon}_g \tilde{E}_\infty c. \quad (17)$$

2.3. Diffuse double layer: first approximation

In the experiments with the apparatus sealed from the ambient air [5], but not those with it open to the atmosphere [5, 14], surfactants were absent, and the surface charge was extremely small. We therefore ignore the Stern layer and specific adsorption of ions [12]. If the diffusivity of ion i is D_i , and \mathbf{u} is the fluid velocity, the ions move under the influence of electric and thermodynamic forces with velocity \mathbf{v}_i given [11] by

$$\mathbf{v}_i = \mathbf{u} - D_i \left\{ \beta^2 z_i \nabla \phi + (1/n_i) \nabla n_i \right\}. \quad (18)$$

As $z_1 = -z_2 = 1$ and $\tilde{n}_{1\infty} = \tilde{n}_{2\infty} = 1$, it is convenient to work with N , the dimensionless total number density of ions, and P , the dimensionless volume charge density times $2\tilde{\lambda}^2$, because

$$N = \tilde{n}_1 + \tilde{n}_2, \quad (19)$$

$$P = \tilde{n}_1 - \tilde{n}_2 = 2\tilde{\lambda}^2 \tilde{\rho}_E = -2\beta^2 \nabla_\lambda^2 \tilde{\phi}, \quad (20)$$

by Poisson's equation. Gouy-Chapman theory ignores \mathbf{v}_i, \mathbf{u} and ϕ_ℓ , and assumes a plane surface, *i.e.* $\tilde{\lambda} \rightarrow 0$; exact solutions and their small- $\tilde{\zeta}$ approximations are given by

$$\begin{aligned} \tilde{\phi} &= \tilde{\phi}_0 \equiv -2\beta^{-2} S \ln t \\ &= \tilde{\zeta} e^{-y} + \frac{1}{48} \beta^4 \tilde{\zeta}^3 (e^{-3y} - e^{-y}) + O(\tilde{\zeta}^5), \end{aligned} \quad (21)$$

$$\begin{aligned} \tilde{E}_r &= \tilde{E}_{r0} \equiv \beta^{-1} \tilde{\kappa} S (t^{-1} - t) \\ &= \tilde{\kappa} \left\{ \beta \tilde{\zeta} e^{-y} + \frac{1}{48} \beta^5 \tilde{\zeta}^3 (3e^{-3y} - e^{-y}) \right\} + O(\tilde{\kappa} \tilde{\zeta}^5), \end{aligned} \quad (22)$$

$$\begin{aligned} N &= N_0 \equiv t^2 + t^{-2} \\ &= 2 + \beta^4 \tilde{\zeta}^2 e^{-2y} + O(\tilde{\zeta}^4), \end{aligned} \quad (23)$$

$$\begin{aligned} P &= P_0 \equiv S (t^2 - t^{-2}) \\ &= -2\beta^2 \tilde{\zeta} e^{-y} + \frac{1}{24} \beta^6 \tilde{\zeta}^3 (e^{-y} - 9e^{-3y}) + O(\tilde{\zeta}^5), \end{aligned} \quad (24)$$

where $S = \text{sgn}(\tilde{\zeta})$,

$$\begin{aligned} t &\equiv \tanh\left(\frac{1}{2}[y - y_0]\right) \\ &= 1 - \frac{1}{2} \beta^2 |\tilde{\zeta}| e^{-y} + \frac{1}{8} \beta^4 \tilde{\zeta}^2 e^{-2y} \\ &\quad + \frac{1}{96} \beta^6 |\tilde{\zeta}|^3 (e^{-y} - 3e^{-3y}) + O(\tilde{\zeta}^4), \end{aligned} \quad (25)$$

$y_0 = \ln \tanh(\frac{1}{4}\beta^2|\zeta|) = -2 \tanh^{-1} t_0$, and $t_0 = \exp(-\frac{1}{2}\beta^2|\zeta|)$. At $y = 0$, $t = t_0$, $\phi_0 = \zeta$, and

$$\tilde{q}_E = \tilde{q}_{E0} = \tilde{E}_{r00} = (2\tilde{\kappa}/\beta) \sinh \frac{1}{2}\beta^2\tilde{\zeta}, \quad (26)$$

$$N_0 = 2 \cosh \beta^2\tilde{\zeta}, \quad (27)$$

$$P_0 = -2 \sinh \beta^2\tilde{\zeta}. \quad (28)$$

(That $\tilde{q}_E = \tilde{E}_{r00}$ follows from Gauss's theorem applied to the diffuse part of the double layer, in which the charge per unit area of surface is $-q_E$.) These solutions are well-known [11, 13] for the case $\beta = 1$, but the extension to $\beta \neq 1$ is new here.

There are a few experiments with fluid-fluid interfaces to check the accuracy of the Gouy-Chapman approximation in really dilute aqueous solutions. Luo *et al.* [15] studied the interface between tetrabutylammonium bromide at various concentrations in water and 0.01 M tetrabutylammonium tetraphenylborate in nitrobenzene. The approximation improved as the concentration in water was reduced; it was good at 0.01 M. Grahame [13] experimented with the interface between sodium fluoride solutions and mercury. He also pointed out that for a non-metallic particle in a salt solution, the particle surface is analogous to the metallic surface at its electrocapillary maximum, and the potential ϕ_H at the outer Helmholtz plane should be regarded as ζ . As he measured both ϕ_H and $\partial q_{E0}/\partial \phi_H$, the differential capacitance of the double layer, one can check the value of van der Weg's β , because (26) implies that

$$\frac{\partial q_{E0}}{\partial \phi_H} = \beta \varepsilon_l \kappa \cosh \left(\frac{\beta^2 \phi_H}{2\Phi} \right). \quad (29)$$

Grahame's Figs. 11–14 show that the fit of (29) to his experiments improved as the concentration reduced; it was very good at 0.001 M if $\beta = 1$ but not if $\beta = 1/\sqrt{2}$. The usual Gouy-Chapman theory with $\beta = 1$ thus seems likely to be good for the bubbles of Kelsall *et al.* [5] At higher concentrations (0.1 and 0.01 M) the capacitance was higher than the Gouy-Chapman value (29). Pereira *et al.* [16] also found higher capacitances in their work with aqueous LiCl and various organic solvents, but their LiCl concentration in water was always 0.01 M, probably too high for Gouy-Chapman theory to hold.

2.4. Diffuse double layer: second approximation

If v_i , \mathbf{u} and ϕ_ℓ are no longer ignored, then (18)–(20) and the steady-state conditions $\nabla \cdot (n_i v_i) = 0$ and $\nabla \cdot \mathbf{u} = 0$ still hold in the absence of chemical reactions. With

$$Pe = V\lambda(D_1 + D_2)/(2\beta^2 D_1 D_2), \quad (30)$$

$$Pe \tilde{\mathbf{u}} \cdot \nabla_\lambda (N - D_{diff} P) = \nabla_\lambda^2 N + \beta^2 \nabla_\lambda P \cdot \nabla_\lambda \tilde{\phi} - \frac{1}{2} P^2, \quad (31)$$

$$Pe \tilde{\mathbf{u}} \cdot \nabla_\lambda (P - D_{diff} N) = \nabla_\lambda^2 P + \beta^2 \nabla_\lambda N \cdot \nabla_\lambda \tilde{\phi} - \frac{1}{2} NP, \quad (32)$$

where $D_{diff} = (D_1 - D_2)/(D_1 + D_2)$ is between +1 if anions diffuse much faster than cations and -1 if cations diffuse much faster. We also assume that the θ velocity component $u = u_0 s$ to a sufficient approximation in the double layer, for some constant speed u_0 to be found later, and that the r component $u_r = 0$ at $r = a$, so $\tilde{u}_r = -2\tilde{u}_0 \tilde{\lambda} y c$ if $y = O(1)$. In Kelsall *et al.* [5] Pe

was of order 3×10^{-4} , $\tilde{u}_0 Pe$ was of order 0.2, and $\tilde{\lambda}$ and $\tilde{\zeta}^2$ were both of order 10^{-3} , so we ignore terms of order $\tilde{\lambda}^2$ and $\tilde{\lambda}\tilde{\zeta}^2$ by comparison with $\tilde{\lambda}$, and let $\phi = \phi_\ell + \phi_0 + \tilde{\lambda}\phi_1$, $N = N_0 + \tilde{\lambda}N_1$, $P = P_0 + \tilde{\lambda}P_1$. Then

$$\tilde{\mathbf{u}} \cdot \nabla_\lambda = \frac{\tilde{u}_0 \tilde{\lambda}}{\beta} \left(-2y c \frac{\partial}{\partial y} + s \frac{\partial}{\partial \theta} \right), \quad (33)$$

$$\tilde{\phi}_\ell = -\tilde{E}_\infty \left(1 + \tilde{\lambda} y + \frac{1}{2} [1 + \tilde{\lambda} y]^{-2} \right) c, \quad (34)$$

$$\begin{aligned} \nabla_\lambda \tilde{\phi} = \mathbf{e}_r \left(-3\tilde{\lambda}^2 E_\infty y c + s [t - t^{-1}] + \tilde{\lambda} \frac{\partial \tilde{\phi}_1}{\partial y} \right) \\ + \mathbf{e}_\theta \left(\frac{3\tilde{\lambda} \tilde{E}_\infty}{2\beta} s + \frac{\tilde{\lambda}}{\beta} \frac{\partial \tilde{\phi}_1}{\partial \theta} \right). \end{aligned} \quad (35)$$

The terms of order $\tilde{\lambda}$ in (20), (31) and (32) reduce to a system of linear ordinary differential equations, with θ acting as a parameter, and f' indicating $\partial f/\partial y$ for any function f :

$$N_1'' = 4\beta^2 \tilde{\zeta} D_{diff} \tilde{u}_0 Pe c y e^{-y}, \quad (36)$$

$$P_1' - P_1 = -4\beta \tilde{\zeta} \{1 + \tilde{u}_0 Pe c y\} e^{-y}, \quad (37)$$

$$\beta^2 \tilde{\phi}_1'' = -\frac{1}{2} P_1 + 2\beta \tilde{\zeta} e^{-y}, \quad (38)$$

As all three of N_1 , P_1 , $\tilde{\phi}_1$ must vanish as $y \rightarrow \infty$, the solutions are

$$N_1 = 4\beta^2 \tilde{\zeta} D_{diff} \tilde{u}_0 Pe (y + 2) e^{-y} c, \quad (39)$$

$$P_1 = \beta \tilde{\zeta} e^{-y} \{ \tilde{u}_0 Pe (y^2 + y) c + 2y + A \}, \quad (40)$$

$$\tilde{\phi}_1 = \beta^{-1} \tilde{\zeta} e^{-y} \left\{ -\frac{1}{2} \tilde{u}_0 Pe (y^2 + 5y + 8) c - y - \frac{1}{2} A \right\}, \quad (41)$$

$$\tilde{E}_{r1} = \tilde{\kappa} \tilde{\zeta} e^{-y} \left\{ -\frac{1}{2} \tilde{u}_0 Pe (y^2 + 3y + 3) c + 1 - y - \frac{1}{2} A \right\}, \quad (42)$$

where A may depend on θ but not on y . The terms involving c in (39)–(42) express the polarization of the double layer by convective diffusion of ions in the flow around the bubble; polarization by the applied field itself would appear in higher-order terms. The free surface charge density \tilde{q}_E is

$$\tilde{q}_E = -\frac{\tilde{\kappa}}{2\beta} \int_0^\infty (1 + \tilde{\lambda} y/\beta)^2 (P_0 + \tilde{\lambda} P_1) dy \quad (43)$$

$$= \tilde{q}_{E0} + \tilde{\zeta} \left\{ 1 - \frac{1}{2} A - \frac{3}{2} \tilde{u}_0 Pe c \right\} + O(\tilde{\lambda} \tilde{\zeta}). \quad (44)$$

According to Derjaguin and Dukhin [17] $\phi_+ - \phi_-$ is independent of θ , and q_E retains its equilibrium value q_{E0} , around a non-conducting rigid particle. If we make the same assumptions for a bubble on which $u_0 \neq 0$, then

$$A = 2 - 3\tilde{u}_0 Pe c, \quad (45)$$

$$\tilde{\phi}_g = \left(-\frac{3}{2} \tilde{E}_\infty - \frac{5}{2} \beta^{-1} \tilde{\lambda} \tilde{\zeta} \tilde{u}_0 Pe \right) \tilde{r} c + \tilde{\zeta} + \tilde{\chi}, \quad (46)$$

$$\tilde{E}_{rg} = \left(\frac{3}{2} \tilde{E}_\infty + \frac{5}{2} \beta^{-1} \tilde{\lambda} \tilde{\zeta} \tilde{u}_0 Pe \right) c, \quad (47)$$

$$\tilde{E}_{r1} = O(\tilde{\kappa} \tilde{\zeta} y) \text{ as } y \rightarrow 0, \quad (48)$$

$$\tilde{q}_B = -\tilde{\varepsilon}_g \tilde{E}_{rg}. \quad (49)$$

The transition from liquid to gas is not really a mathematical discontinuity but occupies 0.4 to 0.9 nm [18–20]. Also, some anions (e.g. F^-) are repelled to distances of that order from the

interface, while others (e.g. ClO_4^-) accumulate there [20, 21]. As even 0.9 nm is much smaller than λ , and $y = 0$ is taken to be the location of the bound charge q_B , we take the free surface charge q_E to be at $y = y_q$ where $|y_q| \ll 1$, and explore the consequences of $y_q < 0$, $y_q = 0$, and $y_q > 0$. Let the normal field be E_{r+} , E_{r-} on the liquid and gas sides of q_B , where $y \rightarrow 0$ through positive and negative values respectively, and E_{rq+} , E_{rq-} on the liquid and gas sides of q_E . Then $E_{rq+} = E_{r00}$ if $y_q \geq 0$ and $E_{r+} = E_{r00}$ if $y_q \leq 0$, while (47) gives $E_{rq-} = E_{rg}$ if $y_q \leq 0$ and $E_{r-} = E_{rg}$ if $y_q \geq 0$. Gauss's theorem gives the remaining E_r values in Table 1. They are needed for calculating the force on the bubble.

Table 1: Dimensionless normal electric field components on each side of $y = y_q$ and $y = 0$ for various values of y_q . \tilde{E}_{r00} is given in (26), \tilde{E}_{rg} in (47).

Hypothesis	\tilde{E}_{rq+}	\tilde{E}_{rq-}	\tilde{E}_{r+}	\tilde{E}_{r-}
$y_q < 0$	$\tilde{E}_{r00}/\tilde{\epsilon}_g + \tilde{E}_{rg}$	\tilde{E}_{rg}	\tilde{E}_{r00}	$\tilde{E}_{r00}/\tilde{\epsilon}_g + \tilde{E}_{rg}$
$y_q = 0$	\tilde{E}_{r00}	\tilde{E}_{rg}	\tilde{E}_{r00}	\tilde{E}_{rg}
$y_q > 0$	\tilde{E}_{r00}	0	0	\tilde{E}_{rg}

2.5. Electrical force on the bubble and double layer

Because E_r changes rapidly across the double layer, the radial component of electrostatic force on the ions in the double layer does not cancel out even though the net charge due to q_E and ρ_E does. However E_θ varies very little across the double layer. At the surface $y = 0$, $E_\theta = -(1/a)\partial\phi/\partial\theta$, and we may ignore any difference between that and $E_{\theta q+}$ or $E_{\theta q-}$. If we put

$$I_r = 2 \int_1^{\tilde{b}} \tilde{r}^2 \tilde{\rho}_E \tilde{E}_r d\tilde{r} = \beta^{-1} \tilde{\kappa} \int_0^\infty \tilde{r}^2 P \tilde{E}_r dy, \quad (50)$$

$$I_\theta = 2 \int_1^{\tilde{b}} \tilde{r}^2 \tilde{\rho}_E \tilde{E}_\theta d\tilde{r} = \beta^{-1} \tilde{\kappa} \int_0^\infty \tilde{r}^2 P \tilde{E}_\theta dy, \quad (51)$$

the dimensionless electrical force \tilde{F}_E on the bubble and its double layer [22, p.251] is calculated from

$$\tilde{F}_E = \tilde{F}_{Er} + \tilde{F}_{E\theta} + \pi \int_0^\pi (I_r c s + I_\theta s^2) d\theta, \quad (52)$$

where

$$\tilde{F}_{Er} = \pi \int_0^\pi \left\{ \tilde{q}_E (\tilde{E}_{rq+} + \tilde{E}_{rq-}) + \tilde{q}_B (\tilde{E}_{r+} + \tilde{E}_{r-}) \right\} c s d\theta, \quad (53)$$

$$\tilde{F}_{E\theta} = -2\pi \int_0^\pi (\tilde{q}_E + \tilde{q}_B) \tilde{E}_{\theta+} s^2 d\theta. \quad (54)$$

Now (52) requires only the part of I_r that is an odd function of c , and the part of I_θ that is an even function of c . They are

$$I_{r,\text{odd}} = \left\{ -6\tilde{\zeta} \tilde{E}_\infty (1 + \tilde{\lambda} \beta^{-1}) + \frac{31}{1536} (\tilde{\zeta}^4 - \tilde{\zeta}^5) \tilde{\kappa} \tilde{u}_0 Pe \right\} c, \quad (55)$$

$$I_{\theta,\text{even}} = \left\{ 3\tilde{q}_E \tilde{E}_\infty (1 - \tilde{\lambda} \beta^{-1}) + \tilde{\zeta}^2 \tilde{u}_0 Pe (8\beta^2 - \frac{9}{4}\beta) \right\} s, \quad (56)$$

when terms thousands of times smaller than the leading terms have been neglected. Table 1 and (52)–(56) then imply that

$$\tilde{F}_E = \begin{cases} \pi \tilde{q}_E (1 - \tilde{\epsilon}_g) (\tilde{E}_\infty + \frac{5}{3} \beta^{-2} \tilde{\lambda}^2 \tilde{q}_E \tilde{u}_0 Pe) & \text{if } y_q \leq 0, \\ 0 & \text{if } y_q > 0, \end{cases} \quad (57)$$

Kelsall *et al.* [5] used $\tilde{F}_E = 4\pi \tilde{q}_E$. Baygents and Saville [9] showed that $\tilde{F}_E = 0$ if all the free charge is in the liquid phase. Our result agrees in that case, which helps check the algebra.

3. Fluid mechanics

3.1. Outside the double layer

If compressibility of both liquid and gas may be ignored we may write

$$u = \frac{1}{rs} \frac{\partial \psi}{\partial r}, \quad (58)$$

$$\tau = \frac{\eta r}{s} \frac{\partial}{\partial r} \left(\frac{1}{r^2} \frac{\partial \psi}{\partial r} \right) - \frac{\eta}{r^3} \frac{\partial}{\partial \theta} \left(\frac{1}{s} \frac{\partial \psi}{\partial \theta} \right), \quad (59)$$

where u is the θ -component of velocity, τ is the shear stress, and ψ is the stream function. We now convert to dimensionless variables. The experiments were done with low Reynolds numbers, and the electric charge density may be ignored outside the double layer, so if either $\tilde{r} < 1$ or $\tilde{r} \geq \tilde{b}$ then

$$L^2 \tilde{\psi} = \left(\frac{\partial^2}{\partial \tilde{r}^2} + \frac{1}{\tilde{r}^2} \frac{\partial^2}{\partial \theta^2} - \frac{c}{s \tilde{r}^2} \frac{\partial}{\partial \theta} \right) \tilde{\psi} = 0. \quad (60)$$

If \tilde{U} is the dimensionless downward velocity of the distant fluid relative to the bubble, solutions sufficient for our purposes are that in the liquid

$$\tilde{\psi} = \left(\frac{1}{2} \tilde{U} \tilde{r}^2 + \alpha_1 \tilde{r} + \alpha_2 \tilde{r}^{-1} \right) s^2, \quad (61)$$

$$\tilde{u} = \left(\tilde{U} + \alpha_1 \tilde{r}^{-1} - \alpha_2 \tilde{r}^{-3} \right) s, \quad (62)$$

$$\tilde{\tau} = 6\alpha_2 \tilde{r}^{-4} s, \quad (63)$$

and in the gas

$$\tilde{\psi} = \left(\alpha_3 \tilde{r}^4 + \alpha_4 \tilde{r}^2 \right) s^2, \quad (64)$$

$$\tilde{u} = \left(4\alpha_3 \tilde{r}^2 + 2\alpha_4 \right) s, \quad (65)$$

$$\tilde{\tau} = 6\alpha_3 \tilde{\eta}_g \tilde{r} s, \quad (66)$$

where the α_i are dimensionless constants. The dominant terms far from the bubble are a uniform stream \tilde{U} , and a Stokeslet of strength α_1 related to the dimensionless external upward force \tilde{F} on the bubble and its double layer by

$$\tilde{F} = -8\pi \alpha_1 = \tilde{F}_E + \tilde{F}_G, \quad (67)$$

where \tilde{F}_E is the electrical contribution to \tilde{F} from Section 2.5 above, and \tilde{F}_G is the gravitational contribution given by

$$\tilde{F}_G = \frac{4}{3} \pi (\rho_\ell - \rho_g) g a^3 / F. \quad (68)$$

3.2. Fluid mechanics in the diffuse double layer

In the diffuse double layer $y = O(1)$, and (20) and (26) with $\tilde{\lambda} = 1/\tilde{\kappa} \ll \tilde{b} - 1 \ll 1$ lead to

$$\frac{\partial}{\partial y} (\tilde{r}^2 \tau) = \frac{1}{2} \beta^{-1} \tilde{\kappa} \tilde{r} P \frac{\partial \tilde{\phi}}{\partial \theta}, \quad (69)$$

$$\begin{aligned} \therefore \frac{\tilde{r}^2 \tau - \tilde{b}^2 \tau_b}{s} &= \tilde{\kappa} \tilde{E}_\infty \left\{ \frac{3}{2} \beta \tilde{\zeta} e^{-y} + \frac{1}{32} \beta^5 \tilde{\zeta}^3 (3e^{-y} - e^{-3y}) \right\} \\ &\quad - \frac{3}{2} \tilde{E}_\infty \tilde{\zeta} e^{-y} + \frac{1}{4} \tilde{\zeta}^2 \tilde{u}_0 Pe (y^2 + 6y + 8) e^{-2y} \\ &\quad + \frac{1}{32} \beta^4 \tilde{E}_\infty \tilde{\zeta}^3 (3ye^{-3y} - ye^{-y} + e^{-3y} - e^{-y}) \\ &\quad + O(\tilde{\lambda}) + O(\tilde{\kappa} \tilde{\zeta}^5) + O(\tilde{\zeta}^4). \end{aligned} \quad (70)$$

Terms involving the product sc in stresses and velocities have been omitted here and subsequently because they have no effect on the electrophoretic mobility. Instead, they give a quadrupolar velocity field [23, 24].

Eq. (70) with $y = 0$ gives the shear stress difference across the diffuse double layer in the liquid, but we also need the shear stress difference across the surface itself. In dimensionless form that is

$$\tilde{\tau}_M - \tilde{\tau}_m = -\tilde{\nabla}_s \tilde{y} - (\tilde{q}_E + \tilde{q}_B) \tilde{E}_\theta. \quad (71)$$

The solutions of Kelsall *et al.* [5] were clean enough and dilute enough for us to ignore $\tilde{\nabla}_s \tilde{y}$. By (16) and (49), $\tilde{q}_B \tilde{E}_\theta \propto sc$, so we omit it, while $\tilde{q}_E \tilde{E}_\theta$ cancels out the largest term in (70) but not all of them. The changes in shear stress, θ -velocity and stream function across the whole double layer can then be found from $\partial \tilde{u}/\partial y = \beta^{-1} \tilde{\lambda} \tilde{\tau}$ and $\partial \tilde{\psi}/\partial y = \beta^{-1} \tilde{\lambda} \tilde{u}$. We write them in terms of variables independent of θ , $\tilde{\tau}_{DL}$, \tilde{u}_{DL} and $\tilde{\psi}_{DL}$, given by

$$\begin{aligned} \tilde{\tau}_{DL} &= (\tilde{\tau}_b - \tilde{\tau}_m) / s \\ &= \frac{3}{2} \tilde{E}_\infty \tilde{\zeta} + \frac{1}{2} \tilde{\zeta}^2 \tilde{u}_0 Pe + O(\tilde{b} - 1) + O(\tilde{\lambda}) + O(\tilde{\zeta}^3), \end{aligned} \quad (72)$$

$$\tilde{u}_{DL} = (\tilde{u}_b - \tilde{u}_m) / s = \frac{3}{2} \tilde{E}_\infty \tilde{\zeta} + O(\tilde{\lambda}) + O(\tilde{\zeta}^5), \quad (73)$$

$$\tilde{\psi}_{DL} = (\tilde{\psi}_b - \tilde{\psi}_m) / s^2 = O(\tilde{\lambda}). \quad (74)$$

If the $O(\cdot)$ terms in (72)–(74) are all negligible, we may put $\tilde{\psi} = 0$ at $\tilde{r} = 1$ in both liquid and gas. Then (61)–(66) give

$$\begin{pmatrix} \frac{1}{2} & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \\ 1 & -1 & -4 & -2 \\ 0 & 1 & -\eta_g & 0 \end{pmatrix} \begin{pmatrix} \tilde{U} \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix} = \begin{pmatrix} -\alpha_1 \\ 0 \\ \tilde{u}_{DL} - \alpha_1 \\ \frac{1}{6} \tilde{\tau}_{DL} \end{pmatrix}, \quad (75)$$

and (67) and (71)–(74) give

$$\tilde{U} = \frac{\tilde{F}(1 + \tilde{\eta}_g)/(2\pi) - \frac{2}{3} \tilde{\tau}_{DL} + 2\tilde{\eta}_g \tilde{u}_{DL}}{2 + 3\tilde{\eta}_g}, \quad (76)$$

$$\tilde{u}_b = \frac{\frac{1}{2} \tilde{U} - \frac{1}{3} \tilde{\tau}_{DL} + \tilde{\eta}_g \tilde{u}_{DL}}{1 + \tilde{\eta}_g} s, \quad (77)$$

$$\tilde{u}_m = \frac{\frac{1}{2} \tilde{U} - \frac{1}{3} \tilde{\tau}_{DL} - \tilde{u}_{DL}}{1 + \tilde{\eta}_g} s, \quad (78)$$

$$\tilde{u}_0 = \frac{\frac{1}{2} \tilde{U} - \frac{1}{3} \tilde{\tau}_{DL} - \frac{1}{2} (1 - \tilde{\eta}_g) \tilde{u}_{DL}}{1 + \tilde{\eta}_g}, \quad (79)$$

if we put $\tilde{u}_0 = \frac{1}{2} (\tilde{u}_b + \tilde{u}_m) / s$. When $\tilde{E}_\infty = 0$, \tilde{F} is purely gravitational, so by (3), (68) and (76),

$$\tilde{U} \left\{ 1 + \frac{\tilde{\zeta}^2 Pe}{6(1 + \tilde{\eta}_g)(2 + 3\tilde{\eta}_g)} \right\} = \frac{\tilde{F}_G(1 + \tilde{\eta}_g)}{2\pi(2 + 3\tilde{\eta}_g)} = \tilde{U}_{RH}, \quad (80)$$

to leading order. Hence \tilde{U} is less than the Rybczyński-Hadamard value \tilde{U}_{RH} , but by an undetectably small amount as Pe was of order 3×10^{-4} and $\tilde{\zeta}^2$ was of order 10^{-3} in the experiments. Physically, the reduction in \tilde{U} is due to the motion of the bubble sweeping ions around the surface, which requires work to be done.

Some of the electrophoretic experiments [5] were done with E_∞ adjusted to keep bubbles of various sizes at rest. For that case, (76) gives the dimensional surface charge to leading order as

$$q_E = \begin{cases} -\frac{4(\rho_\ell - \rho_g)ga}{3(1 - \tilde{\epsilon}_g)E_\infty} = q_E(0), \text{ say,} & \text{if } y_q \leq 0, \\ \frac{\beta(1 + \tilde{\eta}_g)(1 - \tilde{\epsilon}_g)}{2(1 + 3\tilde{\eta}_g)} \tilde{\kappa} q_E(0) & \text{if } y_q > 0, \end{cases} \quad (81)$$

We note that $y_q > 0$ gives q_E much larger than $q_E(0)$, because $\beta \geq 1/\sqrt{2}$, $\tilde{\epsilon}_g \ll 1$ and $\tilde{\kappa} \gg 1$.

In other experiments, Kelsall *et al.* allowed the bubbles to rise with various values of E_∞ , measured U , and reported the values of E_∞ and u_E , the electrophoretic mobility given by

$$E_\infty u_E = U - U_{RH}, \quad (82)$$

where U_{RH} was defined in (3). If one uses those results to deduce q_E from (57) and (76) for $y_q \leq 0$, then

$$q_E = \frac{(4 + 6\tilde{\eta}_g)\eta_\ell u_E}{(1 - \tilde{\epsilon}_g)(1 + \tilde{\eta}_g)a - (2 - 6\tilde{\epsilon}_g)\lambda/\beta}, \quad (83)$$

which is close to four times the value from Kelsall *et al.* [5, Eq. (7)] If $y_q > 0$,

$$q_E = \frac{(2 + 3\tilde{\eta}_g)\beta\kappa\eta_\ell u_E}{3\tilde{\eta}_g - 1}, \quad (84)$$

which has the wrong sign for a bubble with $\eta_g \ll 1$ but agrees with the classical rigid-body result [11] if $\eta_g \rightarrow \infty$ and $\beta = 1$. Eqs. (81), (83) and (84) suggest that the surface charge on a clean-surfaced bubble is at or on the gas side of the permittivity change, but on a rigid body it is on the liquid side of the permittivity change. Fig. 2 shows the variation of $q_E a / \eta_\ell u_E$ with κa according to (83) for gas bubbles in Kelsall *et al.*'s water ($\tilde{\eta}_g = 0.0235$, $\tilde{\epsilon}_g = 0.0128$) and for rigid bodies ($\tilde{\eta}_g \rightarrow \infty$), for both $\beta = 1$ and $\beta = 1/\sqrt{2}$, and according to Booth's theory [8]. Two graphs are used because of the wide variation in values of $q_E a / \eta_\ell u_E$ and the small difference between some of them if $\kappa a \gg 1$, which is the domain of validity of our theory.

4. Comparison with Experiment

Fig. 3 shows the surface charges q_E obtained from (81) with $U = 0$, and experiments [2, 5] on bubbles of various sizes (56

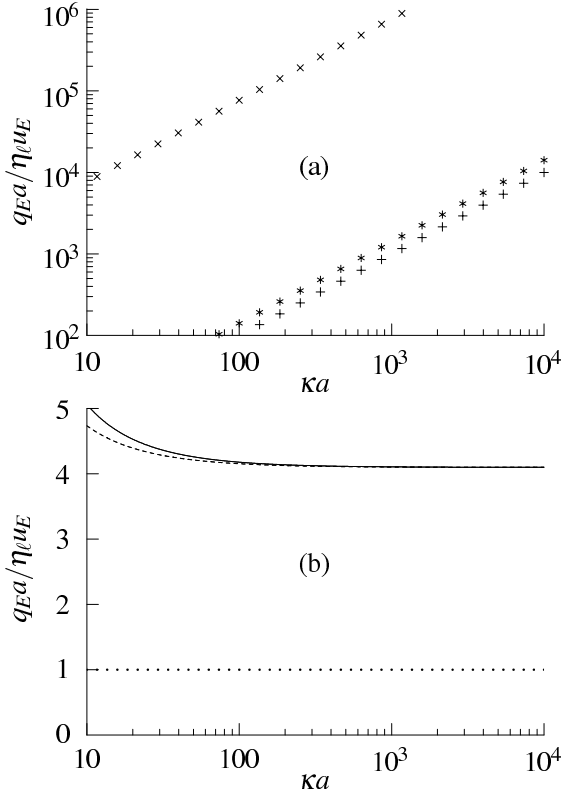


Figure 2: Plots of $q_{Ea}/\eta_l u_E = \tilde{q}_E/\tilde{u}_E$ against $\kappa a = \bar{\kappa}$ for gas bubbles in water according to various theories. (a) Log-log plot for $q_{Ea}/\eta_l u_E \gg 1$; (b) Log-linear plot for $q_{Ea}/\eta_l u_E \leq 5$. Symbols: \times , ref. [8]; $*$, rigid body, $\beta = 1/\sqrt{2}$; $+$, rigid body, $\beta = 1$; solid lines, (83), $\beta = 1$; dashed, (83), $\beta = 1/\sqrt{2}$; dotted: ref. [5].

to 91 μm diameter) held at rest by suitable imposed fields E_∞ . They are plotted only for the three pH values closest to 7 (*i.e.* 5.4, 6.5, 8.3) in order that the approximations of the theory may be good; even at pH 5.4 the concentrations of Na^+ and ClO_4^- are still about 25 times those of any other ions in the solution. These results vary systematically with pH but not much with bubble size, as one would hope, but they are about three times the values that Kelsall *et al.* obtained by a different method independent of their measurements of electrophoretic mobility. That was finding what concentration of the cationic surfactant DoTAB (dodecyltrimethylammonium bromide) would reduce the mobility to zero in a 10^{-4} M solution of NaClO_4 at pH 6.9. They found $q_E = -17.4 \mu\text{C m}^{-2}$, but one wonders how reliable the method is. When Brandon *et al.* [1] used it they found $q_E = -460 \mu\text{C m}^{-2}$ for 10^{-3} M NaNO_3 at pH 6.9. Neither the difference between NaNO_3 and NaClO_4 nor the difference between 10^{-3} M and 10^{-4} M can explain a factor of over 26 in surface charge and hence electrophoretic mobility, according to Figs. 3 and 4 of Kelsall *et al.* [5]

Fig. 4 shows the surface charges obtained from (83), and experiments [3, 5] in which the electric field was fixed at various values ($E_\infty = 1.92, 4.0, 6.0, 8.1, 10.0$ kV/m) and pH = 6.32. The values are spread more widely than those in Fig. 3;

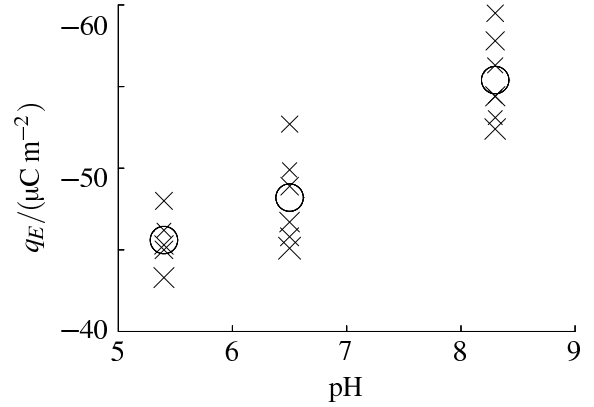


Figure 3: Surface charge q_E deduced from Yurdakul's data [2, 5] on bubbles of various sizes held at rest, at pH 5.4, 6.5 and 8.3. \times , with size \propto bubble diameter: individual bubble results. Circles: mean surface charge for each pH value.

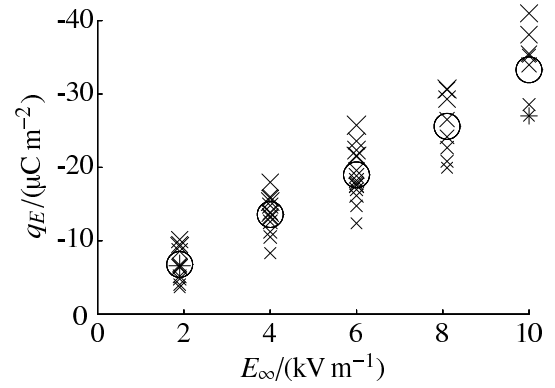


Figure 4: Surface charge q_E deduced from Tang's data [3, 5] on rising bubbles of various sizes at pH 6.32 with $E_\infty = 1.92, 4.0, 6.0, 8.1, 10.0$ kV/m. \times (or $+$ where two bubbles would have superposed symbols), with size \propto bubble diameter: individual bubble results. Circles: mean surface charge for each E_∞ value.

Fig. 5 shows that they are proportional to E_∞ instead of being independent of it.

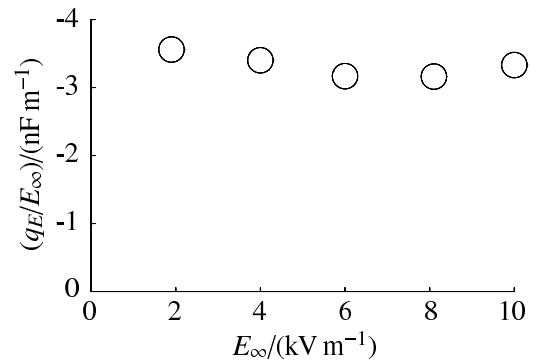


Figure 5: Mean surface charge q_E divided by field strength E_∞ , plotted against E_∞ , from Fig. 4.

Although Kelsall *et al.* [2, 3, 5] worked with solutions of several salts, Figs. 3 and 4 use their data only for NaClO₄ because that is the one for which they reported pH values. The calculations for both figures were done with $\beta = 1$ and $y_q \leq 0$. Changing β to $1/\sqrt{2}$ would make very little difference to either figure, but a positive value of y_q would give impossibly high surface charges, by (81).

5. Conclusions

The electrophoretic results show that the surface charge on an oxygen bubble in an uncontaminated NaClO₄ solution is not on the liquid side of the change in permittivity from liquid to gas, but it could be either exactly at the change or on the gas side of it. This is consistent with the known [25] structure-breaking property of ClO₄⁻ ions, which tend to disrupt the network of hydrogen bonds between the H₂O molecules and so are repelled from the interior of the liquid to the surface [26].

Grahame's [13] work with differential capacitance of a double layer strongly suggests that $\beta = 1$, *i.e.* that traditional Gouy-Chapman theory for the double layer is better than with $\beta = 1/\sqrt{2}$. That conflicts with van der Weg's [10] analysis of experiments by Hills and Ives with a hydrogen-calomel cell [27, 28]. Measuring the surface charge q_E by bubble electrophoresis does not help to resolve this conflict because q_E turns out to be almost independent of β . Of course the zeta potential deduced from q_E is approximately proportional to β , by (26), so it would be divided by $\sqrt{2}$ on van der Weg's [10] hypothesis, but that would require independent measurements of q_E and ζ .

The theory of this paper and those in [5, 8, 9] all give q_E independent of E_∞ , but the experiments with moving bubbles had u_E and hence q_E increasing with E_∞ . Those experiments also had $u_E \propto (a - a_0)$ instead of $u_E \propto a$, with a_0 of the same order as a : it varied from 28 μm at $E_\infty = 1.92 \text{ kV/m}$ to 15 μm at $E_\infty = 10 \text{ kV/m}$. The experimenters themselves said (without detailed calculation) that double-layer polarization was responsible, but Section 2.4 suggests that its effect would have been far too small. Perhaps the sides of the electrophoresis cell became charged [6]. If so, there would have been an electro-osmotic flow near the sides, with a return flow in the middle of the cell where the bubbles were. However Kelsall *et al.* [5] thought that their cell was large enough for that effect to be ignored. It was indeed ignorable, but because of the shapes of the cell and electrodes rather than their size. Yurdakul [2, Fig. A1] showed that the electric field E_w at the cell walls was at most 20% of that between the electrodes, so in the experiments $|E_w| < 2 \text{ kV/m}$. If the zeta potential at the glass walls was ζ_w , the electro-osmotic velocity there would have been $U_w = E_w \epsilon_t \zeta_w / \eta_t$, [11] so $|U_w| < 0.1 \text{ mm/s}$ if $|\zeta_w| = 60 \text{ mV}$. It seems not to have been measured. The electro-osmotic velocity at the position of a bubble would have been even smaller than $|U_w|$, but the actual bubble velocities were much larger (except in the experiments with bubbles held at rest). The experimental variation of q_E with E_∞ and the largeness of a_0 still await their explanation.

Also awaiting an explanation is the generally larger q_E values for bubbles held at rest than for those allowed to rise. Fig. 3

suggests that q_E would have been near $-50 \mu\text{C m}^{-2}$ at pH 6.32, but none of the values in Fig. 4 is as high as that. The zeta potential deducible from the experimental q_E is about -2 mV , which is much smaller than in other work [29] suggesting about -60 mV , but in that other work the gas-liquid interface was not surfactant-free.

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