A THEORETICAL INVESTIGATION OF BUBBLE ELECTROPHORESIS①

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ABSTRACT The fluid movement inside and outside a bubble rising in a liquid medium was investigated by taking the interfacial tension gradient and the potential variation along the bubble surface into account, then the potential distribution within the double layer and the electroneutral area outside the bubble was determined in order to get the normal and tangential potential gradient on the surface; Finally, a formula describing the electrophoretic mobility was reached, which is obviously distinct from that for solid particles and has been found to be in consistence with experimental results.

Key words bubble fluid recirculation interface potential electrophoretic mobility

1 INTRODUCTION

The electrokinetic phenomenon of liquid-gas interface is one of the important properties of bubbles. The thorough and correct understanding of the phenomenon has essential significance in a wide variety of industrial processes, and, therefore, has been an attempt of a series researchers since Quincke[1] who first studied the electrophoresis of bubbles as early as 1861. However, although many experimental observations have been made (Brandon[2] and Yurdakul[3], in their Ph. D. theses, gave good reviews on the experimental aspects of the subject, respectively), the theoretical investigation of the bubble electrophoresis is still far from satisfactory. As a consequence, researchers[4-7] had to calculate values of ζ-potential from their experiments by invoking the classical Smoluchowski equation[8] which, strictly speaking, is valid only for solid-liquid interface.

According to Overbeek and Wiersema[9], the only detail theoretical analysis of the electrokinetic phenomena of nonrigid particles, including liquid drops and gas bubbles, was given by Booth[10]. Neglecting the relaxation effect, Booth derived the electrophoretic mobility of a fluid sphere with arbitrary electrical conductivity on the basis of Herry's work[11] of solid particles. Following three cases have been discussed in Booth's paper: (a) no electric charge within the sphere; (b) uniform distribution of charge throughout the sphere and (c) ionic double layer in the sphere. The case (a) refers to the bubble situation. Unfortunately, the application of Booth's result to bubbles led to the conclusion that bubbles have zero electrophoretic mobility, which is contradictory to the observed facts. Booth himself attributed the contradiction to the variation of the viscosity which was not taken into account in his work as the double layer was traversed. Sengupta[12] introduced surface conductivity to modify Booth's theory and found that the bubble electrophoretic mobility is inversely proportional to the bubble size, which, however, is inconsistent with the experimental observations[2, 13]. Jordan and Taylor[14] also discussed the internal circulation correction for the case in which there is no charge within the sphere. They corrected Henry's formula by multiplying the formula with a factor which is 3/2 for bubbles, on the basis of the fact that the Stokes' friction is decreased by the internal motion inside the sphere. Jordan and Taylor's result contradicts Booth's but also does not agree with

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the observed facts.

Raygents and Saville[15] examined the electrophoresis of drops and bubbles and found some new aspects which are different from solid particles by computing the electrophoretic mobility as a function of the ζ-potential and several other parameters.

In this paper, we are going to start our work by investigating the fluid movement inside and outside a bubble rising in an electrolyte solution. As expected, the bubble rise rate was found to be related with the properties of the bubble and medium, the interfacial tension gradient and the potential variation on the bubble surface. Therefore, an effort was made to work out the potential distribution within the areas outside the bubble, including the double layer and the electrical neutrality zone. Finally, the bubble electrophoretic mobility was derived when the external electrical field parallel to the bubble rise direction is applied. The formula is certainly different from that of solid particles but will be proved elsewhere to be consistent with experimental results[16].

2 FLUID MOVEMENT INSIDE AND OUTSIDE A BUBBLE

Let us consider a bubble of radius a rising at rate of U in an infinite liquid medium. The adopted sphere polar coordinates with its origin at the bubble center and moving together with the bubble is shown in Fig. 1.

For the bubble above, we make following assumptions:

(a) The fluid velocities in both sides of the bubble are so small, i. e. the flow Reynolds number $Re < 1$, that the inertial force can be neglected;

(b) The electrical double layer immediately outside the bubble is much thinner than the bubble radius (a), i. e. $\kappa a \gg 1$, here κ is the Debye- Huckel parameter and its reversal is the measured thickness of double layer;

(c) Compared with the outside solution, the dielectric constant and conductivity of the bubble itself are negligible;

(d) The direction of the external electrical field is parallel to the z-axis, therefore the potential and ionic concentrations outside the bubble are symmetric about z-axis in both presence and absence of the external field;

(e) What we are concerned here is just the situation in which there exists internal circulation within the bubble, as for that of no circulation where the bubble behaves like a solid particle is not considered in this paper.

Fig. 1 The Adopted Sphere Polar Co- ordinates

Then the Navier- Stokes equation governing the flow of fluids inside and outside the bubble can be written as

$$\eta \nabla^2 \boldsymbol{u} - \nabla p_m = \rho \nabla \Psi \qquad (1)$$

$$\nabla \cdot \boldsymbol{u} = 0 \qquad (2)$$

where $\boldsymbol{u}$ is the fluid velocity vector, η is the fluid viscosity, ρ the net charge density in the liquid, Ψ the potential distribution, p_m the modified pressure being related with the fluid static pressure, p, as[17]

$$p_m = p + s g r \cos\theta \qquad (3)$$

where s the fluid density and g the gravitational acceleration.

The solution of equations (1) and (2) is

$$\varphi = \left[\frac{A}{r} + Br + Cr^2 + Dr^4\right] \sin^2\theta \qquad (4)$$

where φ is Stokes function which has relation with the normal and tangential velocity compo-

nents as follows:

$$u_r = \frac{1}{r^2\sin\theta}\frac{\partial\varphi}{\partial\theta}$$

and $$u_\theta = -\frac{1}{r\sin\theta}\frac{\partial\varphi}{\partial r} \quad (5)$$

The arbitrary constants A, B, C, and D are determined by boundary conditions[10, 18].

as $r \to \infty$

$$\frac{\varphi}{r^2} \to -\frac{U\sin^2\theta}{2} \quad (6)$$

as $r = 0$ (7)

$$\frac{1}{r^2\sin\theta}\frac{\partial\varphi'}{\partial\theta} < \infty, \quad -\frac{1}{r\sin\theta}\frac{\partial\varphi'}{\partial r} < \infty \quad (8)$$

as $r = a$

$$\frac{\partial\varphi'}{\partial\theta} = \frac{\partial\varphi}{\partial\theta} = 0 \quad (9)$$

as $r = a$

$$\frac{\partial\varphi'}{\partial r} = \frac{\partial\varphi}{\partial r} \quad (10)$$

as $r = a$

$$\frac{\eta'}{r}\frac{\partial}{\partial\theta}\left(\frac{1}{r^2\sin\theta}\frac{\partial\varphi'}{\partial\theta}\right) - \eta' r\frac{\partial}{\partial r}\left(\frac{1}{r^2\sin\theta}\frac{\partial\varphi'}{\partial r}\right) = \frac{\eta}{r}\frac{\partial}{\partial\theta}\left(\frac{1}{r^2\sin\theta}\frac{\partial\varphi}{\partial\theta}\right) - \eta r\frac{\partial}{\partial r}\left(\frac{1}{r^2\sin\theta}\frac{\partial\varphi}{\partial r}\right) + \frac{\varepsilon_r}{4\pi r}\frac{\partial\Psi}{\partial r}\frac{\partial\Psi}{\partial\theta} + \frac{1}{r}\frac{\mathrm{d}\gamma}{\mathrm{d}\theta}$$

$$p' - 2\eta'\frac{\partial}{\partial r}\left(\frac{1}{r^2\sin\theta}\frac{\partial\varphi'}{\partial\theta}\right) = p - 2\eta\frac{\partial}{\partial r}\left(\frac{1}{r^2\sin\theta}\frac{\partial\varphi}{\partial\theta}\right) + \frac{2\gamma}{r} - \frac{\varepsilon_r}{8\pi}\left(\frac{\partial\Psi}{\partial r}\right)^2 \quad (11)$$

where γ is the interface tension, ε_r the relative fluid dielectric constant and the superscript $'$ refers to the fluid inside the bubble. The terms of electrical stress across the interface in Eqs. (10) and (11) are derived from the Maxwell stress tensor[10]. It should be noted that the electrical stresses in the bubble side, being included in ref. [10], have been neglected in the equations above because the dielectric constant of bubbles is much smaller than that of the solution outside. In addition, the term $\mathrm{d}\gamma/\mathrm{d}r$, not taken into account in ref. [10] but is included here.

From Eqns. (6) ~ (10), we determine the eight arbitrary constants as:

$$\left.\begin{aligned} A' &= 0 \\ B' &= 0 \\ C' &= \frac{3U}{4} - \frac{ga^2(s-s')}{6\eta} + \frac{aF}{3\eta} \\ D' &= -\frac{3U}{4a^2} + \frac{g(s-s')}{6\eta} - \frac{F}{3\eta a} \\ A &= \frac{Ua^3}{2} - \frac{ga^5(s-s')}{6\eta} + \frac{a^4F}{3\eta} \\ B &= \frac{ga^3(s-s')}{6\eta} - \frac{a^2F}{3\eta} \\ C &= -\frac{U}{2} \\ D &= 0 \end{aligned}\right| \quad (12)$$

where

$$F = \frac{1}{\sin\theta}\frac{\varepsilon_r}{4\pi a}\left(\frac{\partial\Psi}{\partial r}\frac{\partial\Psi}{\partial\theta}\right)_{r=a} \quad (13)$$

In order to obtain more information of the fluid movements inside and outside the bubble and, furthermore, the electrophoresis mobility of the bubble, one must find out the potential distribution within the double layer. Meanwhile, it is necessary to point out that the potential should be proportional to $\cos\theta$ because F must be independent of θ (Noting that C', D', A and B are constants), in other words the terms containing higher power of $\cos\theta$, i.e. $\cos^2\theta$, $\cos^3\theta$ and so on can be neglected during the derivation of potential distribution, which is important for simplifying the analysis.

3 POTENTIAL DISTRIBUTION OUTSIDE THE BUBBLE

There are three regions to be considered when the potential distributions are investigated. One is the region within the bubble where no charge exists and Laplace equation is applied, second is the double layer area in which the net charge density ρ is not zero and then Poison-Laplace equation is satisfied, the third region is outside the double layer where the electrical neutrality can be assumed approximately[19, 20] and Laplace equation is invoked again.

Because the potential inside the bubble is not included in Eqn. (13), what we are concerned here is just the areas outside. The relevant potential equations are

$$\nabla^2 \Psi_1 = -\frac{4\pi\rho}{\varepsilon_r}, \quad a \leqslant r \leqslant a + \chi \tag{14}$$

$$\nabla^2 \Psi_2 = 0, \quad r \geqslant a + \chi \tag{15}$$

here Ψ_1 and Ψ_2 are the potential distributions within and outside the double layer with thickness χ, respectively. In general, the potential can be divided into two parts, one is the equilibrium potential, Ψ^0, dependent only on r and denoting the potential distribution when the bubble is supposed to be at rest; the other is the perturbation $\delta\Psi$, a function of both r and θ, caused by bubble rise, internal circulation and external electrical field. This kind of method has been widely used in the theoretical study of electrophoresis for solid particles. Additionally, it is very reasonable to assume that the disturbance term is rather small compared to the equilibrium one[19], which will be important for our analysis later.

The potentials within and outside the double layer are restricted by following boundary conditions:

$$\text{as } r = a + \chi \quad \Psi_1^0 = \Psi_2^0 \text{ and } \delta\Psi_1 = \delta\Psi_2, \tag{16}$$

$$\text{as } r = a + \chi \quad \left.\begin{aligned} \frac{\partial \Psi_1^0}{\partial r} &= \frac{\partial \Psi_2^0}{\partial r} \\ \frac{\partial \delta\Psi_1}{\partial r} &= \frac{\partial \delta\Psi_2}{\partial r} \end{aligned}\right| \tag{17}$$

$$\text{as } r \to \infty, \quad \Psi_2^0 = 0 \tag{18}$$

$$\text{as } r \to \infty, \quad \frac{\partial \delta\Psi_2}{\partial r} = -E\cos\theta \tag{19}$$

where E is the external electrical field which, in direction, is parallel to the bubble rise velocity vector. When giving these conditions, we have assumed that the dielectric constants of solutions in and out the double layer are the same and that the double layer thickness χ is much smaller than bubble radius a.

In the electrical neutrality area outside the double layer, both equilibrium potential and perturbation satisfy Laplace equation and the solutions are easily obtained as

$$\Psi_2^0 = \frac{\beta_1}{r} \tag{20}$$

$$\delta\Psi_2 = \frac{\beta_2}{r^2}\cos\theta - Er\cos\theta \tag{21}$$

where β_1 and β_2 are arbitrary constants and only the terms with $\cos\theta$ are remained according to the analysis at the end of previous section.

As for the potential distribution Ψ_1 within the double layer, the procedure to the solution is much more complicated. The exactly analytical solution of Eqn. (14) can be approached only when the potential Ψ_1 is independent of θ and its value is small. However, what we are concerned here is the general case. With the assumption that the net charge density within the double layer is composed of equilibrium and perturbation parts, the equilibrium potential gradiant within the double layer is derived as

$$\frac{d\Psi_1^0}{dr} = \pm\left\{\left(\frac{2\Psi_{1a}^0}{a}\right)^2 + \frac{8\pi kT}{\varepsilon_r}\left[\sum n_{i0}\exp\left(\frac{-Z_i e\Psi_1^0}{kT}\right) - \sum n_{i0}\exp\left(\frac{-Z_i e\Psi_{1,a+\chi}^0}{kT}\right)\right]\right\}^{1/2} \tag{22}$$

where Z_i the valence of the i - component, e the electronic charge, n_{i0} the numerical density of i component in the bulk solution, k the Boltzman constant, and T the absolute temperature. The signs before the right side of equation (22) are chosen to be negative as $\Psi_1^0 > 0$ and positive as $\Psi_1^0 < 0$. Because that what we are concerned here is just the potential gradiant (See equation. (13)), the complicated integration of equation (22) is unnecessasry.

As for the potential disturbance $\delta\Psi_1$, it is possible, in many cases, to assume that the absolute of $Ze\,\delta\Psi_1$ is smaller than kT because perturbation potential is very small compared to the equilibrium one[20]. Consequently, the perturbation potential within the double layer is mathematically obtained as follows:

$$\delta\Psi_1 = \alpha_1\frac{\kappa r + 1}{(\kappa r)^2}\exp[-\kappa(r-a)]\cos\theta + \alpha_2\frac{\kappa r - 1}{(\kappa r)^2}\exp[\kappa(r-a)]\cos\theta \tag{23}$$

where α_1 and α_2 are arbitrary constants which together with the constants β_1 and β_2 in Eqns. (20) and (21) can be determined as from bound-

ary conditions:

$$\left.\begin{aligned}
\beta_1 &= 2a\Psi_{1a}^0\\
\beta_2 &= \frac{a^2\delta\Psi_{1am}\exp(\kappa X)}{1+\exp(2\kappa X)} + Ea^3\\
&\quad - E[2a^3(1+\lambda)\exp(\kappa X)\\
&\quad + 3a^2\exp(2\kappa X)/\kappa\\
&\quad - 3a^2/\kappa]/[1+\exp(2\kappa X)]\\
\alpha_1 &= \frac{\kappa a\delta\Psi_{1am}\exp(2\kappa X)}{1+\exp(2\kappa X)}\\
&\quad - E[\kappa a^2(1+\lambda)\exp(2\kappa X) - 3a\exp(\kappa X)]/\\
&\quad [1+\exp(2\kappa X)]\\
\alpha_2 &= \kappa a\delta\Psi_{1am}/[1+\exp(2\kappa X)] -\\
&\quad E[\kappa a^2(1+\lambda) + 3a\exp(\kappa X)]/\\
&\quad [1+\exp(li2\kappa X)]
\end{aligned}\right\} \quad (24)$$

here $\lambda = (K - K')/(2K + K') = 1/2$, K' and K the conductivity of the air and solution respectively.

4 THE ELECTROPHORETIC MOBILITY OF THE BUBBLE

Substituting the Stokes' stream functions inside and outside the bubble, together with the potential distribution outside the bubble, into Eqn. (10) yields, after some manipulations:

$$U = \frac{2ga^2(s-s')(\eta+\eta')}{3\eta(2\eta+3\eta')} - \frac{2\gamma_1}{3(2\eta+3\eta')} \pm \frac{\varepsilon_r(\eta+2\eta')[\delta\Psi_{1am} - Ea(1+\lambda)]}{6\pi\eta(2\eta+3\eta')} \times \left[\frac{8\pi kT}{\varepsilon_r}\left(\sum n_{i0}\exp\left(\frac{-Z_i e\Psi_{1a}^0}{kT}\right) - \sum n_{i0}\right)\right]^{1/2} \quad (25)$$

This equation describes the general relation between bubble rise rate and all factors which have effects on the bubble movement. These factors are bubble radius a, density s' and viscosity η', liquid medium density s, interfacial tension gradient γ_1 ($\gamma_1 = -\mathrm{d}\gamma/\sin\theta\mathrm{d}\theta$), viscosity η, external electrical field E, surface equilibrium potential Ψ_{1a}^0, maximum surface potential perturbation $\delta\Psi_{1am}$ and the properties of electrolytes in solution.

In order to get the formula of electrophoretic mobility, it is necessary to make further analysis to the potential perturbation. In theory, $\delta\Psi_{1am}$ can be regarded as being composed of two parts, $\delta\Psi_{1am}^E$ and $\delta\Psi_{1am}^{NE}$, the former is caused by the external electrical field E and the latter is generated by other factors. If we let

$$U_{NE} = \frac{2ga^2(s-s')(\eta+\eta')}{3\eta(2\eta+3\eta')} - \frac{2\gamma_1}{3(2\eta+3\eta')} \pm \frac{\varepsilon_r(\eta+2\eta')\delta\Psi_{1am}^{NE}}{6\pi\eta(2\eta+3\eta')}\left\{\frac{8\pi kT}{\varepsilon_r} \times \left[\sum n_{i0}\exp\left(\frac{-Z_i e\Psi_{1a}^0}{kT}\right) - \sum n_{i0}\right]\right\}^{1/2} \quad (26)$$

here U_{NE} refers to the bubble rise rate when no electrical field is applied; the electrophoretic mobility u_E, defined as the ratio of the bubble velocity caused by the electrical field, i. e. $U - U_{NE}$, to the field strength E, is derived finally as

$$u_E = (U - U_{NE})/E = \pm\frac{\varepsilon_r(\eta+2\eta')[\delta\Psi_{1am}^E/E - a(1+\lambda)]}{6\pi\eta(2\eta+3\eta')} \times \left\{\frac{8\pi kT}{\varepsilon_r}\left[\sum n_{i0}\exp\left(\frac{-Z_i e\Psi_{1a}^0}{kT}\right) - \sum n_{i0}\right]\right\}^{1/2} \quad (27)$$

where the selective signs are dependent on the surface potential Ψ_{1a}^0, the positive is chosen for $\Psi_{1a}^0 < 0$ and negative for $\Psi_{1a}^0 > 0$. For a symmetric electrolyte, Eqn. (27) can be simplified as

$$u_E = -\frac{\varepsilon_r(\eta+2\eta')}{6\pi\eta(2\eta+3\eta')}\left[\frac{\delta\Psi_{1am}^E}{E} - a(1+\lambda)\right] \times \left(\frac{32\pi n_0 kT}{\varepsilon_r}\right)^{1/2}\sinh\left(\frac{Ze\Psi_{1a}^0}{2kT}\right) \quad (28)$$

where $n_0 = n_{+0} = n_{-0}$, $Z = Z_+ = Z_-$。

Here we are satisfied to point out that the bubble electrophoretic mobility formula derived above can explain a series of experimental facts, such as the dependence of mobility on the bubble size, the external field direction and the strength. The comparison and detailed discussion of Eqn. (27) will be reported in another paper[16].

5 SUMMARY

The bubble electrophoretic mobility has been an unsolved problem for a quite long time

although some theoretical work has been done since the end of 1940's. In this paper, we try to find a different approach to the problem.

By investigating the fluid movement inside and outside a bubble and analysing the potential distribution within the double layer and the electroneutral area, a new formula describing the electrophoretic mobility of the bubble is derived theoretically in the paper.

The expression of the bubble electrophoretic mobility advanced here is importantly different from the traditional ones of particles. The new formula can explain the experimental results, such as the dependence of electrophoretic mobility on the direction and intensity of the external electrical field. Also the formula relates the mobility with bubble size, which is a fact found by carefully designed experiments[2, 3].

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