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ORIGINAL CONTRIBUTION

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Improvement of the spinning electrophorometer for zeta potential measurements

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Abstract In this study, bubbles are held by centripetal force at the center of a rotating cylinder filled with an aqueous solution. Their velocities along the axe of rotation, after application of an electrophoretic force, are used for the calculation of the so-called electrokinetic potential. But this process necessitates the elimination of the electro-osmosis which occurs on the interior sides of the glass cylinder by superposing a concurrent force on the bubble. Efficiency of DEAE-Dextran reticulated with 1,4 Butanediol Diglycidyl Ether can be tested by the observation of a cloud of latex microspheres injected in the interior of the tube and allowed to move in respect with the application of an electric field. The experimental control of these velocity profiles proves the adequacy of the polymer for many cases such as surfactant solutions, presence of electrolytes, utilization with moderate pH.

The dynamic interpretation of the electrophoretic motion of bubbles is possible by considering that small ones behave like rigid spheres moving in a rotating fluid. In the second part of this paper and in a previous publication, we have experimentally proved that the use of the theoretical expressions of the forces involved for rigid spheres is justified for small bubbles. So, the electrokinetic potential can be expressed versus the velocity, leading to possible interpretations of the adsorption on gas-water interfaces.

Key words Electrokinetic potential – gas-aqueous interface – spinning cylinder

Introduction

The electrical charge on air bubbles is an important factor when considering industrial processes such as flotation or purification [1]. At the beginning of the century researchers captured a gas bubble along the axis of a rapidly rotating horizontal glass tube filled with water [2, 3]. The extremities of the tube were sealed with metal electrodes and the speed of the bubble movement along the axis was measured as a function of the applied voltage. These experiments have been criticized because the applied electric field results in a electro-osmotic flow inside of the tube, as well as creating an electrophoretic motion of the bubble [4–6]. In this paper our purpose is to show that the vanishing of the electro-osmotic flow in a rotating tube filled with an aqueous solution is possible under various conditions [7], smearing the tube surface with a long polymer chain in order to neutralize the surface charges. Furthermore, we describe the hydrodynamic behavior of a bubble in this rotational system and give an example of a theoretical interpretation of mobility measurements.

Electro-osmosis control

Usually, glass–water interfaces exhibit negative charges because the dissociation constants of silica groups give a predominant importance of SiO^- sites for pH > 3 [8]. With respect to the electroneutrality condition, the water near the inner side of a cylindric capillary is positively charged. When this system is plunged into an electric field, important motions of the fluids near the sides and at the center of the rotating tube make the electrophoretic measurements of bubbles difficult to perform. Figure 1 shows a schematic representation of the apparatus used with the dramatic influences of the electro–osmotic flows.

For the elimination of the electro–osmosis, the choice of a long polymeric chain molecule leans on the following considerations:

i) Neutralization of negative sites by an ion exchange process [9] ;

ii) Extent of the plane of shear beyond the double layer [10] ;

iii) Nonionic character of the chain.

Diethyl amino ethyl dextran hydrochlorid satisfies i) considering the exchange between the N^+ of the DEAE part of the molecule and the SiO^- sites of the glass. Dextran allows the extent of the plane of shear ii) beyond the double layer, but a reticulation of all the graft molecules is necessary and will be realized with 1,4-Butanediol diglycidyl ether [11]. The molecule with its two parts is represented in Fig. 2.

The efficiency of the coating is easily controlled by using polystyrene latex microspheres [11]. Visualization of their mobility in an electric field for several planes of viewing gives us the mobility profile that characterizes the electro–osmotic flow. The comparison of the profiles between uncoated and coated tubes filled with a solution of anionic surfactant (hexadecyl benzene sulfonate: 8ΦC16) is shown in Fig. 3.

For the uncoated tube, the profile is characteristic of the electro–osmotic phenomena. The positive charge of water near the capillary walls is given under the two stationary levels which represent the only planes where the electro-osmosis does not exist. Furthermore, the negative charge of the wall is increased by the presence of surfactant molecule adsorbed at the surface. The comeback flow at the center of the tube is due to the closed geometry of our experimental system.

The other profile confirms that treating capillaries with DEAE-Dextran suppressed the electro-osmosis. In this case, the negative charges of the microspheres result from the adsorption of 8ΦC16 on their surface; their intrinsic electrophoretic mobility is equal to

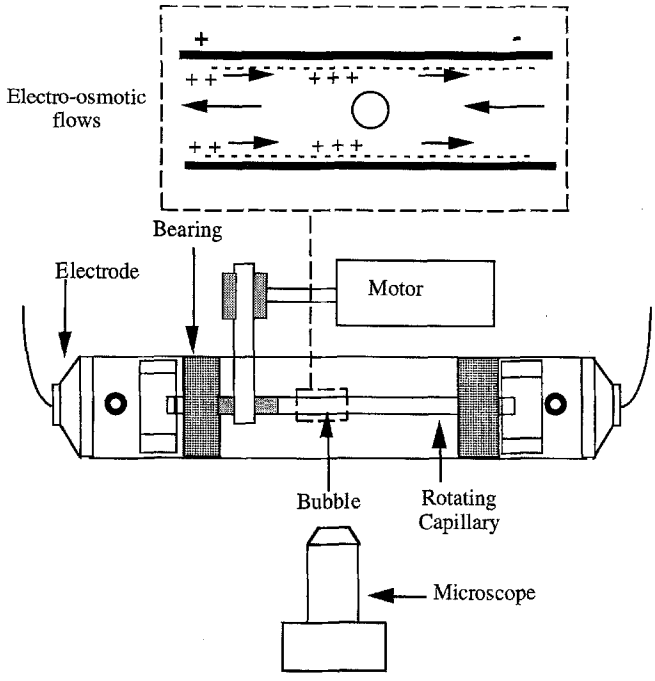


Fig. 1 Apparatus representation and electro-osmosis visualization

$-4\ \mu m \cdot s^{-1} \cdot V^{-1} \cdot cm$. We can compare this value to the $-2\ \mu m \cdot s^{-1} \cdot V^{-1} \cdot cm$ obtained by using water in a tube coated with the same polymer and representing the natural mobility of latex microspheres.

Significantly, this coating is very stable during a period of 3 months. We can use this with other anionic, nonionic, or mixed solutions and add electrolytes without reestablishing the electro–osmosis. Electrophoretic mobility of bubbles can be evaluated without any sort of other electrokinetic phenomenon.

Hydrodynamic behavior of bubbles

When a solid sphere moves along the axis of rotation like in a spinning tube experiment, columns of liquid appear in front and behind the moving sphere and are known as Taylor columns [12]. The regions connecting these columns to the surface of the bubble are called Ekman layers [13, 14]. The forces acting on this shape of fluid all around the surface are not of the magnitude of those observed on a sphere moving in a quiescent liquid. The drag involved is larger and reduces the sphere mobility. Important theoretical and experimental studies of the mobility of a solid sphere in a horizontal rotating fluid have been achieved, and we propose to prove that their main results are applicable for small bubbles when using our apparatus [15]. Outside the Ekman layers we can follow the analysis of

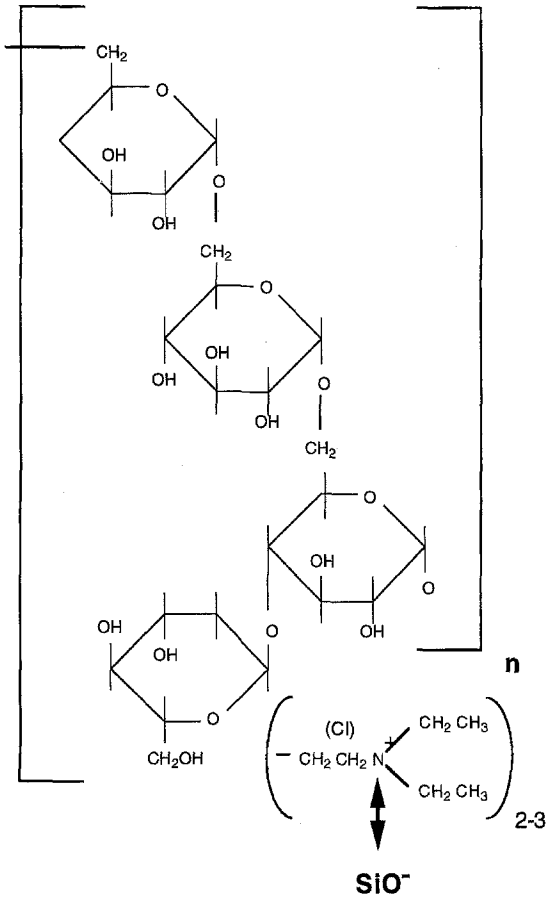


Fig. 2 DEAE molecule for electro-osmosis neutralization

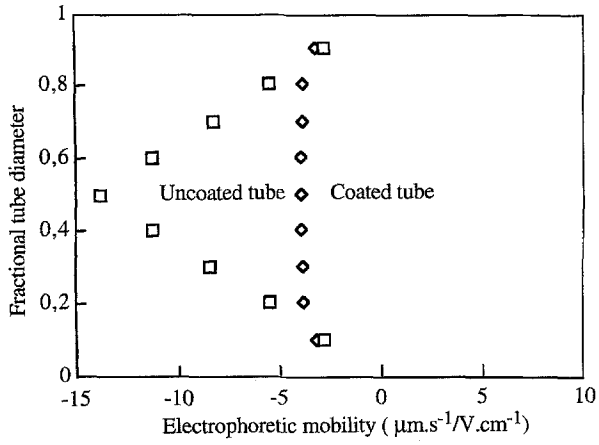


Fig. 3 Electrophoretic mobility ($E = 4000$ V/m) of spherical latex particles (4 μm) for coated and uncoated tubes in a 8ΦC16 aqueous solution ($4 \cdot 10^{-4}$ M)

Moore and Saffman. Using cylindric coordinates (r, θ, z) where $\mathbf{V}(u, v, w)$, we have:

$$-2\Omega v = \rho^{-1}\frac{\partial p}{\partial r} \qquad 2\Omega u = v\left(\frac{\partial^2 v}{\partial r^2} + \frac{1}{r}\frac{\partial v}{\partial r} - \frac{v}{r^2}\right)$$

$$0 = -\frac{1}{\rho}\frac{\partial p}{\partial z} + v\left(\frac{\partial^2 w}{\partial r^2} + \frac{1}{r}\frac{\partial w}{\partial r}\right). \tag{1}$$

Furthermore, the equation of continuity is:

$$\frac{1}{r}\frac{\partial}{\partial r}(ru) + \frac{\partial w}{\partial z} = 0\,. \tag{2}$$

The boundary conditions are $u, v, w \to 0$

when $r^2 + z^2 \to \infty$. (3)

The contribution of the electric field appears in the Ekman compatibility relation:

$$w_{\pm} - U = \pm\frac{1}{2\lambda r}\frac{d}{dr}\left(rv_{\pm}(1+f'^2)^{1/4}\right) + \frac{3\varepsilon E\zeta}{4\mu\lambda r}\frac{d}{dr}\left(\frac{r^2}{a}(1+f'^2)^{1/4}\right). \tag{4}$$

This equation represents the boundary condition of (1) and (2). The first term at the right side of the equality is the derivative of the hydrodynamic flow in the Ekman layer which appears when considering the motion (velocity U) of a spheric particle on the axis of a rotating fluid. The second term represents the derivative of the electroosmotic flow around an immobile charged spheric particle created by the application of the electric field (E). In the following expression we have:

$$z = \pm f(r) = \pm(a^2 - r^2)^{1/2} \quad \text{and} \quad \lambda = \sqrt{\frac{\Omega}{v}}\,. \tag{5}$$

Numeric resolutions of these equations give:

$$U = 3,6\frac{\varepsilon E\zeta}{\mu r\lambda}\,. \tag{6}$$

The experimental conditions are in agreement with the assumptions imposed by Sherwood who resolved the equations presented above [15] and proposed this last equation which is the analogue of the Smoluchowski's equation.

Bubble surface considered like rigid

We have tilted the tube with several inclinations (θ) and measured the rising speed of the bubbles. The well known expression of the rising force on the bubble is

$$F = \frac{4}{3}\pi r^3 \Delta\rho \cdot g \sin\theta. \tag{7}$$

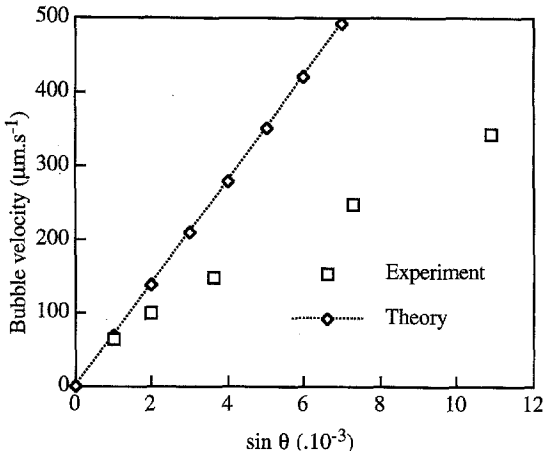


Fig. 4 Bubble velocity ($r/R = 0$, 18, $\Omega = 110$ Rad/s) versus tube inclination

At small Reynolds numbers, the drag on a spherical and rigid particle [16] is represented by:

$$D = \frac{16}{3}\rho\Omega r^3 U \,, \tag{8}$$

with Ω: rotational speed; r: bubble radius; ρ: density; U: bubble velocity.

The comparison between the theoretical predictions of Stewartson (obtained by equaling (7) and (6)) and our experimental results is shown in Fig. 4.

This figure shows that the theoretical prediction for rigid spheres matches the experimental results when $\sin\theta \to 0$. The same deviation can be found with other bubble radii and other rotational speeds. The deviation observed when $\sin\theta > 10^{-3}$ can be interpreted by the increase of the Reynolds number, thus leaving the applicability restriction of the theory when the drag is independent of the viscosity. We have verified that the dependence between U and Ω (with r and θ constant) can be represented by $U = \text{Cste}/\Omega$. The fact that the theoretical results fit our experimental ones is a strong evidence that bubbles behave like rigid spheres moving in an *unbounded* rotating fluid for *small* Reynold's number ($5 \cdot 10^{-3} < R_e < 8 \cdot 10^{-1}$) characteristic of the apparatus.

Length of the tube considered infinite compared with the length of the Taylor columns.

This condition is theoreticaly verified by the expression:

$$h \gg rT^{1/2} \quad \text{with} \quad T = \frac{\Omega\rho r^2}{\mu}$$

h, r: length of the tube and radius of the bubble.

For most measurements, $h = 25 \cdot 10^{-2}$ m and $r \cdot T^{0,5} < 4 \cdot 10^{-4}$ m. The condition is verified.

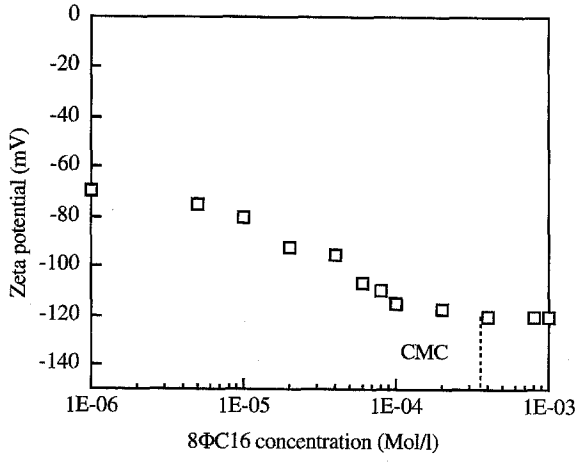
Ekman layers considered small compared with the bubble radius.

We must have $T^{-1} \ll 1$. Our experiments were carried out with $T^{-1} \approx 0,1$. It would be better to increase T, but distortion of the bubble appears when we increase Ω. The stress exerted by the external flow on the bubble is thought to be balanced by a surface tension gradient created by a surface flow that tends to sweep surface impurities. These surface tension gradients are disrupted when we increase r with r/R constant. Hydrodynamic conditions are changed. Thus, the assumption of a rigid sphere becomes unvalid.

Example of application

We have studied the adsorption of 8ΦC16 on air bubbles for various concentrations (Fig. 5). By the application of (5), we have obtained the precedent graph that characterizes the so-called adsorption isotherm. We can note the value of the CMC of the surfactif ($3 \cdot 10^{-4}$ M) when there is saturation of the interface and the potential remains constant. This CMC is in agreement with the one found in the literature [17]. It is to be noted that the zeta potential of the same bubbles in deionized water is -65 mV. Figure 5 shows that the zeta potential reaches this value when the concentration of surfactant is low.

Fig. 5 Zeta potential ($E = 4000$ V/m) of an air bubble ($r/R = 0$, 18, $\Omega = 110$ Rad/s) for different anionic surfactant (8ΦC16) concentrations



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Conclusion

The technique of the spinning tube electrophorometer is a good attractive device for measuring the ζ-potential at gas–liquid or liquid–liquid interfaces by elimination of the electro–osmotic flows for every condition of adsorption studied. The alteration of the classic apparatus used at the beginning of the century is possible by deposing DEAE-Dextran on the surface of the capillary. Furthermore, interpretation of the electrokinetic mobilities with the usual Smolukowski's theory is still possible, but considering the hydrodynamic conditions, is dramatically different compared with those of a motion of a spherical particle in a quiescent liquid. We have followed the Moore and Saffman's theory, adapted to the spinning tube electrophorometer by Sherwood. The system has given the justifications of the theoric hypothesis and, above all, the experimental verifications of the final result which unites the electrokinetic mobilities to the so-called zeta potential. Now, the spinning tube can be used for the characterization of the laws governing the adsorption at the gas–liquid interfaces.

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