Rotating Bubble Method for the Determination of Surface and Interfacial Tensions

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A new method for the measurement of surface and interfacial tensions is suggested. The two phases to be investigated are placed in a closed container which is rotated at a known speed about a horizontal axis. Under the influence of the forces of rotation and of surface tension the lighter phase will take the equilibrium shape of an elongated bubble along the axis of rotation. If the length of the bubble is made large compared to the radius, the shape of the bubble can be closely approximated by a circular cylinder with hemispherical ends. For the case of a long bubble expressions are derived for the surface tension as a function of the bubble dimensions and for the shape of the bubble end.

WHEN a closed vessel containing a liquid and a bubble, either of a gas or a lighter, immiscible liquid, is rotated about a horizontal axis, the bubble will tend to find an equilibrium position on the axis of rotation because of the pressure caused by the centrifugal force. As the speed of rotation is increased, the bubble will elongate along the axis until finally it is in the form of a long narrow circular cylinder with rounded ends. For each speed of rotation the bubble will come to an equilibrium shape that is stable and characteristic of that speed. Figure 1 shows photographs of air bubbles in a viscous glucose solution rotated at successively higher speeds. The container is a glass tube held in the chuck of a small lathe. From top to bottom the approximate speeds of rotation are, respectively, 365, 550, 820, and 1250 r.p.m. It will be observed that there are two large bubbles and that as the speed is increased they elongate and become of the same diameter. The small spots between the two larger bubbles are very small bubbles which have not had time to travel through the viscous liquid to the axis of rotation.

If surface tension were absent and an infinitely long container used, the rotating bubble would continue to elongate indefinitely until it became infinitesimally narrow. When surface tension is present, elongation of the bubble under the influence of the forces of rotation continues until these forces are balanced by the opposing forces of surface tension. This equilibrium condition can exist because the force of the rotational field tending to elongate the bubble is proportional to the fourth power of the bubble radius while the opposing surface tension force is proportional to the first power of the radius.

A general mathematical solution for the shape of the bubble is complex, but, if the effects of gravity are neglected and the length of the bubble is assumed to be large compared to the radius, the treatment is simplified. In the latter case the bubble can be closely approximated by a

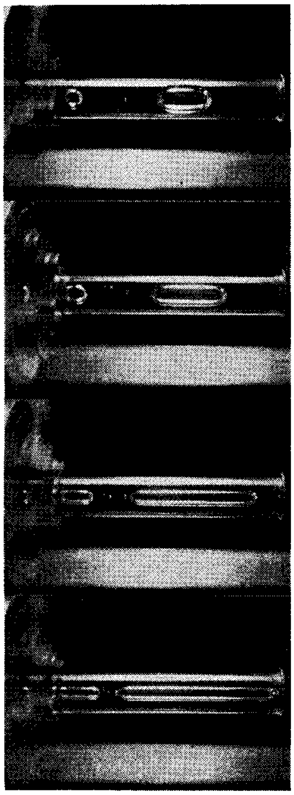

FIG. 1. Bubbles in glucose solution rotated at various speeds.

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cylinder with hemispherical ends. The expression relating the tension of the bubble surface to the angular velocity, the dimensions of the bubble, and the densities of the two phases can be derived in several ways. Probably the simplest method is to set up an expression for the energy of the bubble and to solve for the equilibrium shape in which the total energy is a minimum.

Assume the bubble to be a cylinder of radius, R, length, L, with hemispherical ends and a constant volume, V. Let ρ_1 be the density of the external liquid, ρ_2 be the density of the bubble phase, T be the surface tension of their interface, and ω be the angular velocity. See Fig. 2.

E_s, the contribution of the surface tension to the energy of the bubble, is the product of the surface tension and the total area,

$$E_s = T(2\pi RL + 4\pi R^2). \tag{1}$$

E_r, the energy of the bubble caused by rotation, is obtained by integrating over the volume of the bubble the product of each element of volume and the difference at that point of the pressure between the inside and outside of the bubble. The pressure difference, p, caused by rotation is given by

$$p = \frac{\omega^2 y^2(\rho_1-\rho_2)}{2}, \tag{2}$$

where y is the distance from the axis of rotation. Thus,

$$E_r = \int p\,dV = \frac{(\rho_1-\rho_2)\omega^2}{2} \times \int_0^R y^2[2\pi Ly + 4\pi y(R^2-y^2)^{\frac{1}{2}}]dy. \tag{3}$$

On carrying out the indicated integration we obtain

$$E_r = \frac{1}{4}\pi(\rho_1-\rho_2)\omega^2 LR^4 + \frac{4}{15}\pi(\rho_1-\rho_2)\omega^2 R^5. \tag{4}$$

The total energy of the bubble is then,

$$E = E_r + E_s = \tfrac{1}{4}\pi(\rho_1-\rho_2)\omega^2 LR^4 + \frac{4}{15}\pi(\rho_1-\rho_2)\omega^2 R^5 + T\pi R^2\left(4+\frac{2L}{R}\right). \tag{5}$$

Expressing the length in terms of the radius and volume, differentiating with respect to R at constant volume, and equating to zero for the condition that the energy is a minimum, we find

$$\frac{dE}{dR} = \frac{8}{3}\pi RT - 2\frac{VT}{R^2} - \tfrac{1}{3}\pi(\rho_1-\rho_2)\omega^2 R^4 + (\rho_1-\rho_2)\omega^2 VR. \tag{6}$$

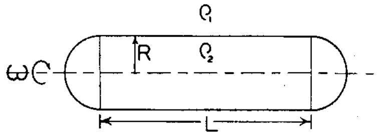

FIG. 2. Bubble shape assumed in derivation.

Substituting for V and solving for T, we obtain

$$T = \frac{(\rho_1-\rho_2)\omega^2 R^3}{4}\left(1+\frac{2R}{3L}\right). \tag{7}$$

It is evident from this expression that as the length of the bubble becomes large in relation to its radius, the surface tension is given by

$$T = (\rho_1-\rho_2)\omega^2 R^3/4. \tag{8}$$

In the case of an infinitely long bubble it is possible to set up a differential equation for the end of the bubble, and, by solving this, to obtain an analytical expression for its form. Consider a longitudinal section of the bubble in x and y coordinates with the vertex of the bubble at the origin and the axis of the bubble coinciding with the x axis. Because the bubble is in equilibrium, the forces at all points are balanced.

Examining the forces acting in the x direction at any circumference, one can see that the resultant force in the x direction caused by pressure acting on the end of the bubble must be balanced by the x component of the surface tension force.

Because of surface tension, at the axis the pressure inside of the bubble is greater than that outside by an amount p_0. At the limiting radius, R, of a long bubble the pressure difference across the surface is the sum of this initial pressure difference at the axis and the contribution of the pressure caused by the centrifugal force. According to the equation of capillarity, this pressure difference across the surface must be equal to the product of the surface tension and the sum of the reciprocals of the radii of curvature. Because the walls of the long bubble are parallel, the one radius of curvature is infinite, hence,

$$p_0-(\omega^2R^2/2)(\rho_1-\rho_2)=T/R. \tag{9}$$

From Eq. (8) for the limiting case of a long bubble,

$$p_0=(3\omega^2R^2/4)(\rho_1-\rho_2). \tag{10}$$

The pressure difference, p existing across any point of the bubble is then the sum of the pressure difference at the axis and that caused by the centrifugal force,

$$p=(\rho_1-\rho_2)\omega^2(\tfrac{3}{4}R^2-y^2/2). \tag{11}$$

The x component of the force on the end of the bubble, F_x, caused by this pressure difference is obtained by integrating over the surface of the bubble from zero to the radius, y, the product of this pressure difference and the projection of this surface on the y, z plane.

$$F_x=(\rho_1-\rho_2)\omega^2\int_0^y\left(\frac{3}{4}R^2-\frac{y^2}{2}\right)2\pi y dy$$
$$=\frac{2\pi(\rho_1-\rho_2)\omega^2}{8}(3R^2y^2-y^4). \tag{12}$$

This force must be balanced by the x component of the surface tension force at that point, F_{xt},

$$F_{xt}=2\pi yT\cos\theta=\frac{2\pi(\rho_1-\rho_2)\omega^2(3R^2y^2-y^4)}{8}. \tag{13}$$

Substituting for $\cos\theta$ in terms of dx/dy,

$$\frac{dx}{dy}=\frac{(\rho_1-\rho_2)\omega^2(3R^2y-y^3)}{8\left(T^2-\left[\frac{(\rho_1-\rho_2)\omega^2}{8}(3R^2y-y^3)\right]^2\right)^{\frac{1}{2}}}. \tag{14}$$

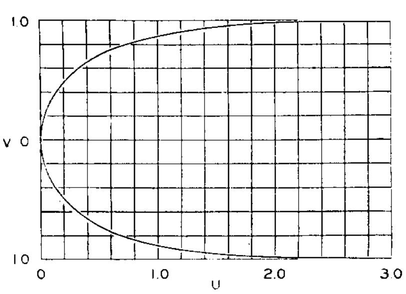

FIG. 3. Graph of equation for shape of end of long bubble.

Letting $x/R=U$, and $y/R=V$, and substituting for T from Eq. (8), we find

$$\frac{dU}{dV}=\frac{V(3-V^2)}{[4-V^2(3-V^2)^2]^{\frac{1}{2}}}. \tag{15}$$

Integrating this we obtain for the shape of the end of the bubble,

$$U=\frac{1}{\sqrt{3}}\left[\ln\frac{2-\sqrt{3}}{2+\sqrt{3}}-\ln\frac{(4-V^2)^{\frac{1}{2}}-\sqrt{3}}{(4-V^2)^{\frac{1}{2}}+\sqrt{3}}\right]+2-(4-V^2)^{\frac{1}{2}}. \tag{16}$$

Figure 3 shows a plot made from this equation. It is interesting to note that at a distance of only 1.4 bubble diameters from the vertex the diameter is but 0.5 percent less than the maximum.

It has already been stated that the bubble in the rotating liquid "tends" to orient itself along the axis of rotation. Were it not for the force of gravity, which is superimposed on the centrifugal force, the bubble would center exactly on the axis of rotation. The effects of gravity become small in two cases. If the viscosity of the liquid is large, the liquid is unable to flow rapidly enough to accommodate itself to the force of gravity, which is constantly changing in direction with reference to the rotating liquid. If increased speeds of rotation are used, the centrifugal force becomes large in comparison with that of gravity.

The degree to which the force of gravity influences the form of the bubble is a function not only of the viscosity, density, and angular velocity, but also the shape of the container. The hydrodynamical problem is complicated. However, it is possible to obtain some understanding of the phenomenon by considering the pressure distribution in the rotating tube of liquid. If the axis of rotation is taken as the origin of an x and y coordinate system perpendicular to the axis of rotation with the ordinate vertical, the variation in pressure can be expressed as a function of x and y. If ρ is the density of the liquid and ω the angular velocity, the pressure p_r at any point due to the rotation is given by

$$p_r=\rho\omega^2(x^2+y^2)/2. \tag{17}$$

The pressure, p_g, caused by gravity is expressed,

$$p_g = -\rho g y. \qquad (18)$$

The sum of these two or the total pressure in the rotating liquid is then,

$$p = [\omega^2(x^2+y^2)/2 - gy]. \qquad (19)$$

The surfaces of equal pressure, which in the absence of other forces would be expected to coincide with the surface of the bubble, are thus cylinders centered about an axis located a distance g/ω^2 above the axis of rotation. This tendency of the bubble to depart from the axis of rotation thus decreases rapidly as the speed of rotation is increased.

The displacement of the axis of the bubble from the axis of rotation acts to retard the rotation of the liquid, and the angular velocity of the bubble is therefore less than that of the container. In Eq. (7) ω is properly the angular velocity of the bubble rather than that of the container. At lower speeds and with liquids of low viscosity an appreciable error is introduced by assuming that they are the same. As the angular velocity is increased, this effect rapidly diminishes. It should be possible to measure the extent of this slip by the use of a stroboscope.

Most of the experimental work thus far has been done on a small metal working lathe with a maximum speed of 3000 r.p.m. This speed, while high enough to give very stable, well-centered bubbles in very viscous solutions, is not high enough for measurements on such mobile liquids as water and alcohol, whose surface tensions are well known. The complicated behavior of these mobile liquids is shown in Fig. 4, which is a photograph of the peculiarly warped bubbles formed in water at 3000 r.p.m.

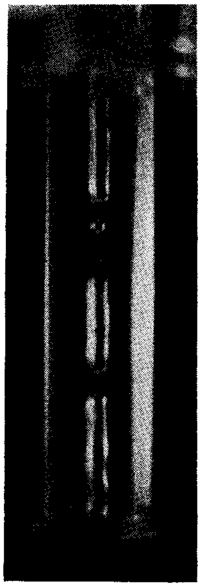

FIG. 4. Air bubbles in water rotating at 3000 r.p.m.

Investigations of this method have been largely qualitative because of the lack of equipment for producing constant and accurately known high speeds of rotation. The only determination thus far is a very rough measurement of the surface tension of liquid Wood's metal at its melting point. The value obtained is liable to considerable error because of contamination of the surface with oxide and the low speed of rotation possible in the lathe. This measurement was made by allowing the molten metal to solidify in a rotating brass tube. Cork stoppers were used to close the ends of the tube, and because the metal did not wet the cork, one end of the bubble was open where it touched the stopper. The diameter of the bubble was determined by inserting drill shanks until a good fit was obtained. This gave a value for the surface tension of about 250 dynes per centimeter.

One of the main advantages of this method for the measurement of surface and interfacial tensions is that the surface of the bubble is closed and no question of contact angle arises. By changing the speed of rotation the area of the bubble may be controlled for investigation of the properties of surface films. The method should be well adapted to measurements on rather viscous substances.

An adequate investigation of this method will involve making measurements of bubble dimensions in liquids of known surface tensions at accurately known speeds ranging from 5000 r.p.m. If the speeds at which the equation holds prove inconveniently high, it is probable that correction factors might be obtained permitting use of the method at more moderate speeds.

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