An Application Of Bubble Shape Theory To The Determination Of Air Transfer Through Adsorbed Surface Films

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The efforts of various investigators (1–4) have led to the development and verification of a theory for the shapes of floating bubbles. The purpose of this note is to apply this information to the data collected by Brown, Thuman and McBain (5) in their attempt to determine the permeability of adsorbed surface films to air by observing from above the radii of floating bubbles as a function of time. As in the work by Brown, Thuman and McBain, it is assumed here that all mass transfer takes place through the thin spherical cap of the floating bubble. In the original work it was assumed that bubbles floating at a surface assumed a spherical shape while floating half-submerged. Thus, the area of one side of the bubble cap always amounted to 50% of the total bubble area. In reality the bubble cap, for the sizes of bubbles considered, amounted to from at most 40% to as little as 1% of the total area.

The permeability k of a bubble dome or cap is defined by the equation

$$-\frac{dn}{dt} = ks\Delta c, \qquad [1]$$

where $-dn/dt$ is the molal flux through the film, s is the dome area, and Δc is the concentration difference across the film. Assuming air to be a perfect gas, expressions for n and Δc are readily developed. Combining these with Eq. [1] we find

$$k = -\frac{\pi r_e^2}{s}\left[\frac{p_0 r_d}{\gamma}\frac{dr_e}{dt} + 4\frac{dr_e}{dt} - \frac{4r_e}{3r_d}\frac{dr_d}{dt}\right], \qquad [2]$$

where r_e is the equivalent bubble radius, r_d is the cap radius, γ is the surface tension, and p_o is the pressure above the bubble. The second and third bracketed terms can be dropped with the introduction of only a negligible error. In order to best utilize the shape information of (4) it is convenient to render the various radii and s dimensionless through division by a and a^2, respectively, where a, the capillary constant, is equal to $(2\gamma/g\Delta\rho)^{1/2}$. Here, g is the acceleration due to gravity and $\Delta\rho$ is the difference in density between the fluid and the gas. Dimensionless variables are written as capital letters. It is convenient to introduce the observed radius r into [2] by multiplying the equation by dr/dr. Thus, we find

$$k = -\frac{\pi a p_0}{\gamma}\frac{R_e^2 R_d}{S}\frac{dR_e}{dR}\frac{dr}{dt}. \qquad [3]$$

From (4) $R_e^2R_d/S$ is a function only of dimensionless bubble size while the relationship between R_e and R is dependent upon both size and the index of refraction. This latter dependence exists because the submerged portion of the bubble, when viewed from above, is seen through an air–fluid interface which is not normal to the line of sight. In the calculations presented an index of refraction of 1.34 was used. For the sake of convenience, $R_e^2R_d/S$ and R_e were expressed as series through the eighth powers of, respectively, R_e and R. The method of least-squares was used to determine the coefficients of these truncated series.

Supposing for the moment that k is constant, Eq. [3] is readily solved. The scatter in the data reported in (5) as well as the lack of measured initial bubble radii in several cases make it convenient to present this solution in the form

$$T = \frac{\gamma kt}{a^2 p_0} + T_s = \pi\int_R^1 \frac{R_e^2 R_d}{S}\frac{dR_e}{dR}\,dR, \qquad [4]$$

where T is the dimensionless time required for a bubble to shrink from a dimensionless observed radius of unity to any radius R. Unity was chosen because no R exceeded this value. T_S , then, represents the nondimenional time, based upon the unity reference radius, at which some particular bubble reached the surface. The last equation thus predicts, for a given index of refraction, a unique relationship between R and T. The problem of finding the appropriate value of k is thus the problem of determining the values of $\gamma k/a^2p_o$ and T_S for which a given set of r–t data is best fitted by this single R–T curve. A least-squares procedure was used to determine these values, using for simplicity an error ϵ defined by

$$\epsilon = \frac{\gamma kt}{a^2 p_0} + T_s - T. \qquad [5]$$

Figure 1 demonstrates the accuracy with which the "universal" R–T curve for an index of refraction of 1.34 fits the data. Table I displays the results obtained for all of the cases reported in (5).

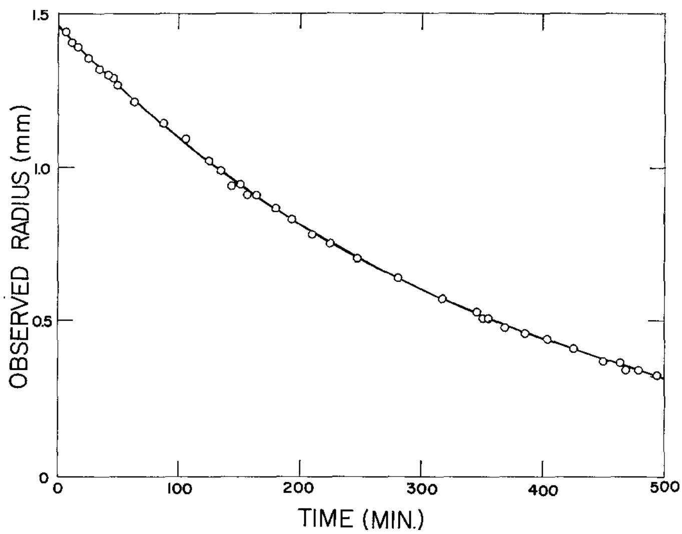

FIG. 1. Observed radius versus time data for a bubble floating at the surface of a 0.1% NaSL solution (5). (—) The theoretical curve for a constant surface tension of 45.7 dyn/cm and a permeability of 0.0758 cm/sec.

TABLE I

CALCULATED PERMEABILITY VALUES FOR VARIOUS SOLUTIONS[a]

Case	Solution	No. of points	Time[b] (min)	Fractional standard deviation[c]	Permeability (cm/sec)	
					Present results	Ref. (5)[a]
1	0.1% NaSL (commercial)	4	75	0.0005	0.0095	0.0037
2	0.1% NaSL	36	495	0.0148	0.0758	0.0099
3	0.1% NaSL, 0.00025% LOH	6	120	0.0031	0.0238	0.0051
4	0.1% NaSL, 0.00025% LOH	6	81	0.0013	0.0155	0.0030
5	0.1% NaSL, 0.00025% LOH	6	86	0.0003	0.0151	0.0024
6	0.1% NaSL, 0.0005% LOH	10	300	0.0013	0.0156	0.0027
7	0.1% NaSL, 0.002% LOH	17	391	0.0022	0.0144	0.0039
8	0.1% NaSL, 0.008% LOH	14	390	0.0038	0.0166	0.0047
9	0.5% NaSL	11	399	0.0262	0.0957	0.0092
10	0.5% NaSL, 0.01% LOH	11	376	0.0179	0.1052	0.0112
11	0.5% NaSL, 0.02% LOH	5	90	0.0023	0.0974	0.0130
12	0.5% NaSL, 0.025% LOH	8	144	0.0020	0.0221	0.0032
13	0.5% NaSL, 0.03% LOH	11	216	0.0063	0.0161	
14	0.5% NaSL, 0.03% LOH	6	87	0.0014	0.0182	
15	0.5% NaSL, 0.03% LOH	4	54	0.0017	0.0191	
16	0.5% NaSL, 0.04% LOH	4	54	0.0022	0.0222	0.0022
17	0.1% Potassium laurate	7	90	0.0038	0.0082	0.0014
18	0.1% E607L	9	86	0.0033	0.0473	0.0091
19	0.1% Quaternary 0	7	82	0.0060	0.0449	0.0065
20	0.1% Santomerse 3	10	67	0.0086	0.0658	0.0130
21	0.1% Triton X-100	10	88	0.0076	0.2144	0.0150

[a] From the data presented by Brown, Thuman and McBain (5).
[b] This is the time interval during which the bubble was observed.
[c] See text.

using surface tension values reported therein. Since the method of interpretation followed by Brown, Thuman and McBain yielded a significant apparent change in k with time the k values from (5) are initial (first hour) ones. To demonstrate in a reasonably compact way the accuracy with which the "universal" R–T curve fits the data, Table I contains values of a fractional standard deviation, σ', defined by the equation

$$\sigma' = \left[\frac{1}{n}\sum_{i=1}^{n}\left(\frac{r_i - r_{p,i}}{r_{p,i}}\right)^2\right]^{1/2}. \qquad [6]$$

In [6], r_i and $r_{p,i}$ are, respectively, the observed and the predicted radii at t_i.

In light of the results reported by Princen and Mason (6) it is appropriate to comment upon the possible time dependence of k which one can obtain from [3]. Various order polynominal fits of the data were used to accomplish this. The results thus obtained were found to be so highly sensitive to the smoothing procedure followed that no firm conclusion about the time dependence of k could be reached. Conclusions in this area are complicated by the possibility that, in the case of very small bubbles, significant mass transfer might take place through areas other than that of the cap. Somewhat crude estimates of an effective surface area indicate that the assumption of mass transfer through only the bubble cap may well introduce measurable error for bubbles whose dimensionless equivalent radii fall below 0.35.

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