

- SSSR, 68, 1097 (1949).
34. ———, and A. M. Rozen, *Zhur. Fiz. Khim.*, 27, 146 (1953).
 35. Kasatkina, L. A., and V. G. Amerikov, *Kinetics and Catalysis*, 7, 86 (1966).
 36. ——— and A. P. Zuev, *ibid.*, 6, 413 (1965).
 37. Klier, K., and K. Kuchynka, *J. Catalysis*, 6, 62 (1966).
 38. Kuentzel, W. E., *J. Am. Chem. Soc.*, 52, 437 (1930).
 39. *Ibid.*, 445 (1930).
 40. Lamb, A. B., N. C. Bray, and J. C. W. Frazer, *J. Ind. Eng. Chem.*, 12, 213 (1920).
 41. ———, C. C. Scalione, and G. Edgar, *J. Am. Chem. Soc.*, 44, 738 (1922).
 42. ———, and W. E. Vail, *ibid.*, 47, 123 (1925).
 43. Loane, C. M., *J. Phys. Chem.*, 37, 615 (1933).
 44. Long, L. J., D. Eng. thesis, Yale Univ., New Haven, Conn., in preparation.
 45. Marcellini, R. P., R. E. Ranc, and S. J. Teichner, "Actes Congr. Intern. Catalyse, 2e, Paris, 1960," Vol. I, p. 289, Editions Technip, Paris (1961).
 46. Mathieu-Levy, L. S., and M. M. Geloso, *Bull. Soc. Chim. France*, 53, 1039 (1933).
 47. Merrill, D. R., and C. C. Scalione, *J. Am. Chem. Soc.*, 43, 1982 (1921).
 48. Moore, T. E., M. Ellis, and P. W. Selwood, *ibid.*, 72, 856 (1950).
 49. Najbar, M., K. Kuchynka, and K. Klier, *Coll. Czech. Chem. Comm.*, 31, 959 (1966).
 50. Parravano, G., *J. Am. Chem. Soc.*, 75, 1448 (1953).
 51. *Ibid.*, 1452 (1953).
 52. Rienacker, G., and E. Scheve, *Z. Anorg. Allgem. Chem.*, 330, 18, 27, 34 (1964).
 53. Rogers, T. H., C. S. Piggot, W. H. Bahlke, and J. M. Jennings, *J. Am. Chem. Soc.*, 43, 1973 (1921).
 54. Roginskii, S. Z. *Acta Physicochim. URSS*, 9, 475 (1938).
 55. ———, and T. F. Tselinskaya, *Zhur. Fiz. Khim.*, 21, 919 (1947); *Chem. Abstr.*, 42, 2500 (1948).
 56. *Ibid.*, 22, 1360 (1948); *Chem. Abstr.*, 43, 2498 (1949).
 57. Roginskii, S. Z., and Ya. Zeldovich, *Acta Physicochim. URSS*, 1, 554 (1934).
 58. *Ibid.*, 595 (1934).
 59. Rousseau, J., M. V. Mathieu, and B. Imelik, *Bull. Soc. Chim. France*, No. 8, 2608 (1966).
 60. Russell, R. G., personal communication (1966).
 61. Schwab, G.-M., and G. Drikos, *Z. physik. Chem.*, A185, 405 (1940).
 62. Shurmovskaya, N. A., and B. P. Burns, *Zhur. Fiz. Khim.*, 9, 301 (1937).
 63. *Ibid.*, 14, 1183 (1940); 24, 1174 (1950); *Chem. Abstr.*, 49, 2165 (1955).
 64. Vainshtein, F. M., and G. Ya. Turovskii, *Dokl. Akad. Nauk SSSR*, 72, 297 (1950).
 65. Vasil'ev, V. N., S. Yu. Elovich, and L. Ya. Margolis, *Dokl. Akad. Nauk SSSR*, 101, 703 (1955).
 66. Ward, T., *J. Chem. Soc.*, 1244 (1947).
 67. Weiss, M. D., M. Ch. E. thesis, Polytechnic Inst. Brooklyn, New York (1952).
 68. Weisz, P. B., and J. S. Hicks, *Chem. Eng. Sci.*, 17, 265 (1962).
 69. Whitesell, W. A., Ph.D. thesis, Johns Hopkins Univ., Baltimore, Md. (1923).
 70. ———, and J. C. W. Frazer, *J. Am. Chem. Soc.*, 45, 2841 (1923).
 71. Williamson, A. T., *ibid.*, 54, 3159 (1932).
 72. Winter, E. R. S., *Advan. Catalysis*, 10, 218 (1958).
 73. Yoshida, F., D. Ramaswami, and O. A. Hougen, *AIChE J.*, 8, 5 (1962).
 74. Zeldovich, Ya., *Acta Physicochim. URSS*, 1, 449 (1934); *Zhur. Fiz. Khim.*, 6, 234 (1935).

Manuscript received May 9, 1968; revision received September 11, 1968; paper accepted September 11, 1968.

COMMUNICATIONS TO THE EDITOR

A Bubble Growth Experiment for the Determination of Dynamic Surface Tension

CHARLES KIPPENHAN and DAVID TEGELER

University of Washington, Seattle, Washington

A number of techniques have been used for the measurement of dynamic surface tension of water-surfactant solutions (1 to 3). One very simple method, utilizing the phenomena of gas bubble formation on a submerged orifice, has been reported (4) but is difficult to apply because of a complicated analytical model. The process of gas bubbling from a submerged orifice into a pure liquid has been subdivided into three regions, namely, the constant volume (or single bubble) region, a transition zone, and a constant frequency region. The latter two taken together have also been referred to as the *regime of chain bubbling* (5 to 7). This note is based on observations made in the single bub-

ble region.

THE EXPERIMENT

The air bubbles were produced on an orifice which was submerged in a transparent plastic walled tank filled with either distilled water or water-surfactant solution. The particular solution used in this study was distilled water plus 0.08 vol. % of Ultra Wet 60L (Atlantic Refining Company, Los Angeles, California) which exhibited an equilibrium surface tension of 33 dynes/cm. as determined by the DeNouy Tensiometer method (maximum

reduction). The arrangement of the bubbling orifice is shown schematically in Figure 1. The orifice is drilled coaxially into a small cavity bored into a 1/2-in. diameter rod, the orifice end of which is polished to a metallurgical grade microfinish. The cavity is isolated from the air supply train by means of a needle-valve assembly arranged so that the pressure drop across it is orders-of-magnitude greater than the pressure fluctuations associated with the change in bubble size.

Two systems were used in obtaining the data reported, a 0.020-in. orifice in aluminum rod and a 0.040-in. orifice in brass rod. This isolated cavity was connected by means of plastic capillary tubing to a standard medical infusion pump. The plunger of a standard surgical syringe (sizes up to 100 cc.) mounted in the pump is driven by a ram that traverses a lead screw. The speed of the ram is controlled continuously by a rheostat changing motor speed; speed ranges are provided by a gear train. This arrangement produced very constant flow rates over a wide range of values. The frequency of bubble formation was determined by timed visual count at lower flow rates and by visually stopping the bubble train ascending in the liquid by means of a stroboscopic illumination at the higher values. The quotient of the constant flow rate divided by the constant frequency of bubble formation, for any given run, yields the final (detached) bubble volume. Provisions for photography, both still and cinemascopic, completed the experimental arrangement.

The bubble volumes thus obtained are plotted in Figure 2 as a function of corrected volume flow rate. This correction, to account for pressure change from the syringe to the hydrostatic environment in the fluid bulk, assumed the expansion process to be reversible adiabatic. The region of single bubbles, characterized by constant bubble volume for the pure water cases, is of interest here. The experimental fact that bubbles in surfactant solution exhibit an increase in volume, with increasing gas flow rate, is exploited for the determination of dynamic surface tensions.

A static force balance between buoyant force upward and surface tension force downward is solved to yield the effective surface tension value. (A slightly more complicated static model, including a pressure force on the bubble surface area above the orifice, was also examined, but because of the small orifice to bubble diameter ratio, the resulting small correction was ignored.)

In a dynamic situation involving both time and area change, a correlating parameter which suggests itself is the rate of bubble surface area change. It can be simply shown that this quantity, here called the *true area strain rate*, can be computed from flow rate and volume by the relation

$$\dot{\epsilon}(t) = \frac{d \ln S(t)}{dt} = \frac{2}{3} \frac{q}{V(t)} \quad (1)$$

The true area strain rate varies for each bubble from an initial maximum value $\dot{\epsilon}_0$ to a final minimum value $\dot{\epsilon}_{\min}$ at detachment, where

$$\dot{\epsilon}_0 = \frac{8}{\pi} \frac{q}{d_0^3}, \quad \dot{\epsilon}_{\min} = \frac{2}{3} \frac{q}{V_b} = \frac{2}{3} f = \frac{2}{3\tau} \quad (1a)$$

With a steady infusion rate q , the growth process should be linear in time, and this was experimentally verified by analysis of the high speed cinemascope.

It should be noted here that in this case of simple static bubble formation on an orifice by gas injection, the bubble time period is associated with the growth of the bubble from its initial nucleus to final pinch off. (This is in contrast to the formation of bubbles in nucleate boiling where the bubble period consists of two parts, the dwell period

associated with energy requirements for an active site to reinitiate nucleation and the growth period similar to the one pertinent here.) For convenience in correlating the data, the minimum true area strain rate which is two-thirds of the reciprocal period was used.

RESULTS

The surface tensions of interest are shown as the ordinate in Figure 3 and are correlated with the minimum true area strain rate just described. The surface tension of distilled water is constant, but for surfactant solution an increase in the rate of surface deformation results in an increase of the effective surface tension. This effect has led to the use of the term *dynamic surface tension*. As the bubble surface is deformed more rapidly, the number of surfactant molecules that can diffuse from the liquid bulk to the liquid-gas interface during the growth period decreases, thus resulting in higher effective surface tension. The data for the 0.020-in. orifice can best be represented by the solid straight line, which was fitted by least squares; the standard error of estimate bounds is shown by dashed lines. The constants for fitting a second-order polynomial were also calculated, but this representation was rejected on statistical grounds. The additional data for the 0.040-in. orifice, which were obtained while this communication was under review, fall within the scatter band and thus lend greater significance to this technique.

CONCLUSIONS

The technique presented here describes a rather simple procedure for the measurement of dynamic surface tension. The utilization of the single bubble region, and thus the simple static bubble model, allows a very simple physical interpretation of the observed phenomena for a situation closely resembling the technical process of nucleate boiling, where dynamic surface tension is of considerable interest. Since the migration of surfactant molecules to the newly forming interface comes from an essentially undisturbed, and for all intents mathematically

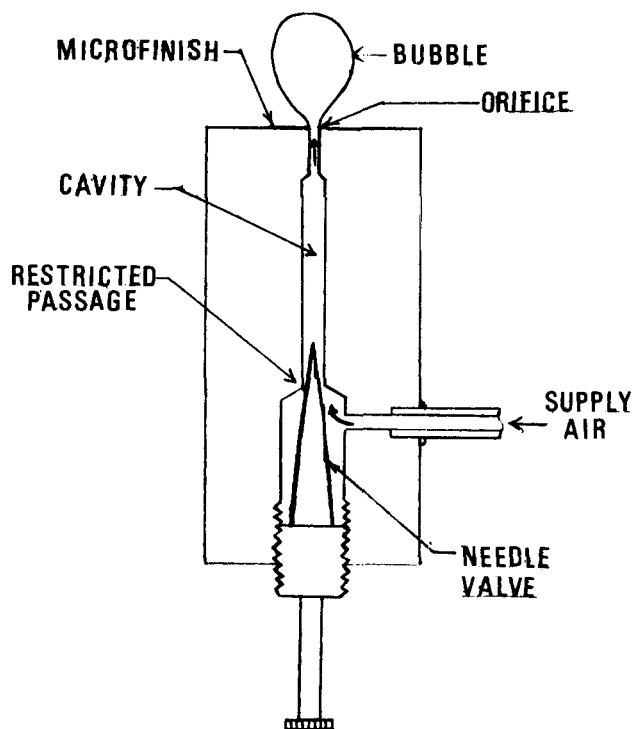


Fig. 1. Needle valve and orifice assembly.

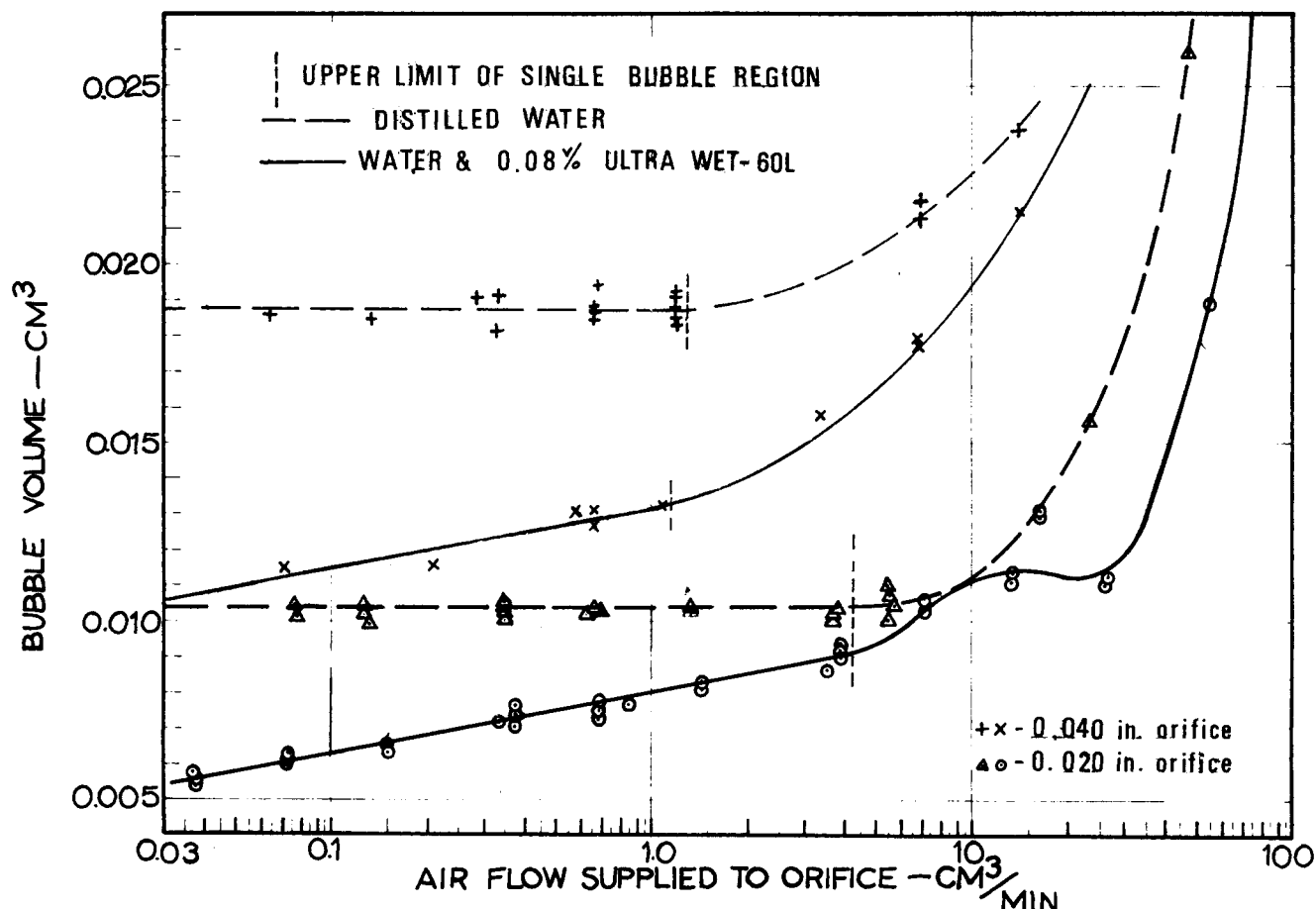


Fig. 2. Plot of average bubble volume vs. air supply rate.

infinite domain, a rather well-defined experiment results. In contrast, the oscillating jet technique discussed by Netzel, Hoch, and Marx (3) and by Sutherland (9) is complicated by the fluid mechanics of a jet expanding from an orifice or elliptical cross-section flow channel. This latter technique requires an empirical correction for the fluid mechanical effects, which results in a pseudo dynamic surface tension even for pure liquids such as water, in order to obtain an apparent dynamic surface tension for surfactant solutions. Similarly, the use of orifice bubbling in the chain bubble region reported by Roll and Meyers (4) and by Hays, Hardy, and Holland (9) requires the use of elaborate theoretical models which include inertial and drag forces that are still poorly understood.

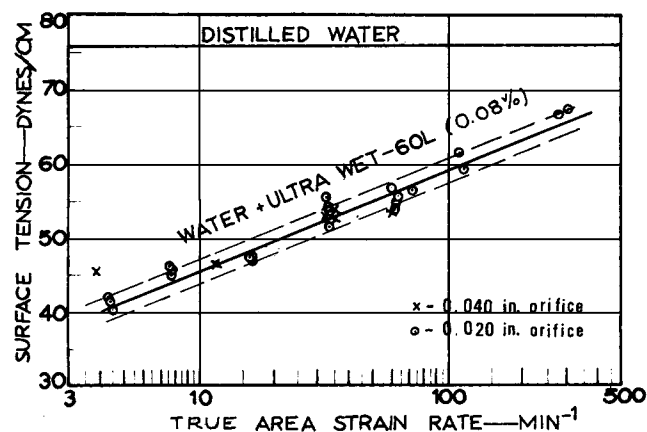


Fig. 3. Plot of surface tension vs. true area strain rate.

ACKNOWLEDGMENT

The early part of this work was performed by the junior author as a National Science Foundation Undergraduate Research Participant in the Department of Mechanical Engineering. His additional work for Master of Science thesis was supported by an Office of Engineering Research Assistantship.

NOTATION

d_0	= orifice diameter
f	= frequency
q	= volumetric air flow rate
S	= bubble surface area
t	= time
V	= bubble volume, V_b (at detachment)
$\dot{\epsilon}$	= true area strain rate
τ	= bubble period

LITERATURE CITED

1. Lange, H., *J. Colloid Sci.*, **20**, 50 (1965).
2. McKeown, J. J., and D. A. Okun, *Air and Water Pollution*, **5**, 113 (1963).
3. Netzel, D. A., G. Hoch, and T. I. Marx, *J. Colloid Sci.*, **19**, 774 (1964).
4. Roll, J. B., and J. E. Meyers, *J. Chem. Eng. Data*, **9**, 256 (1964).
5. Van Krevelen, D. W., and P. J. Hoftijzer, *Chem. Eng. Progr.*, **46**, 29 (1950).
6. Siemes, W., *Chem. Eng. Technik*, **26**, 479, 614 (1954); *Chem. Eng. Sci.*, **5**, 127 (1956).
7. Davidson, Leon, and E. M. Amick, Jr., *AIChE J.*, **2**, 336 (1956).
8. Sutherland, L., *Australian J. Chem.*, **7**, 320 (1954).
9. Hays, W. B., B. W. Hardy, and C. W. Holland, *AIChE J.*, **5**, 319 (1959).