

Measurement of Dynamic Surface Tension in Bubbling Systems

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The static and dynamic surface tension has been measured for aqueous solutions of eleven surface active agents for the purpose of studying the effect of surface tension upon boiling heat transfer. The surfactants have been chosen from the Tween, Aerosol, and Hyonic series. Dynamic surface tension, at $T = 90^{\circ}\text{C.}$, was investigated by observing the volume and frequency for air bubbles forming from a submerged orifice. Static surface tension, at $T = 100^{\circ}\text{C.}$, was measured using a duNouy tensiometer. In all cases, the dynamic surface tension for solutions of these surface active agents was less than the value for pure water, greater than the static value for the same concentration, and was a smoothly decreasing function of concentration.

EARLY IN THE COURSE of an investigation into the effects of surface tension upon boiling heat transfer (4) it was apparent that a method of determining, or at least characterizing, the effective surface tension of a surfactant solution under nonequilibrium conditions was required. Methods of measuring dynamic (nonequilibrium) surface tension are discussed by Schwartz and Perry (5) and include the falling drop, the pulsating jet, and the impinging jet methods. While these methods do measure a dynamic surface tension, it was felt that in this case a device as similar to boiling systems as possible was required.

APPARATUS

The apparatus for determining dynamic surface tension (Figure 1) consisted of a gas train terminating at a brass orifice of known diameter. Volumetric flow control was achieved using an air valve with a constant effluent pressure. The flow rate was determined by noting the time required for a soap bubble to pass between two marks on a volumetric buret, a device known as a "soap-bubble flow-meter." The pressure in the buret was determined with a mercury manometer. A 130 cm. length of nominal $\frac{1}{2}$ mm. ID glass capillary was placed directly behind the orifice to maintain constant flow rate. The orifice was drilled in a piece of brass bar-stock, $\frac{1}{2}$ -inch OD \times $1\frac{1}{8}$ -long; the $\frac{1}{16}$ -inch (0.159 cm.) hole was drilled at the axis.

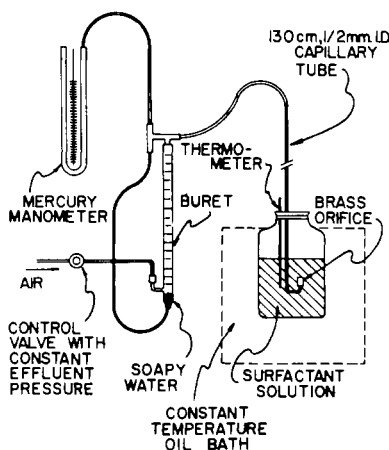


Figure 1. Dynamic surface tension apparatus

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The surface of the orifice was polished with "O" grade emery paper. Bubble frequency was determined using a General Radio Stroboscope. The vessel containing the test liquid was a one gallon glass jar. It was supported inside a constant temperature oil bath capable of maintaining a temperature of $90^{\circ} \pm 1^{\circ}\text{C.}$ within the test jar. A mercury thermometer gave this temperature.

Operating procedure consisted of filling the jar with $2\frac{1}{2}$ liters of water and an appropriate amount of surfactant and adjusting the oil bath heaters until the desired temperature was reached by the liquid in the jar. Data points were taken by noting: bubble frequency, gas flow rate, buret pressure, and liquid temperature.

CALCULATION PROCEDURE

The data consisted of T , the bath temperature ($^{\circ}\text{C.}$); ΔP , the pressure in the gas buret (mm. Hg, gauge); q' , the gas rate in gas buret, at pressure and temperature of buret ($\text{cm.}^3/\text{sec.}$); and f , the bubble frequency (bubbles/minute).

From these data q , the volumetric flow rate through the orifice, was calculated:

$$q = q' \left(\frac{760 + \Delta P}{760} \right) \left(\frac{273 + T}{273 + 25} \right) \quad (1)$$

Equations for the volume of air in the bubble and the diameter of an equivalent spherical bubble are:

$$V = \frac{60q}{f} \quad (2)$$

and

$$D = \left(\frac{6\alpha V}{\pi} \right)^{1/3} \quad (3)$$

where α is a constant factor to correct for water vapor in the bubble as a result of evaporation at the bubble surface during formation. The temperature correction involves the assumption that the gas in the buret was at 25°C. and that the bubble was fed gas at the bath temperature. It can be shown that under conditions of this experiment, the latter assumption was justified.

EQUATIONS

Hayes, Hardy, and Holland (1) and Hughes, Handlos, Evans, and Maycock (2) have analyzed the forces acting on a growing bubble. Their results can be expressed in the following equation:

$$\alpha V \Delta \rho g (1 - \psi) = \pi D_0 \sigma \left(1 - \frac{D_0}{D}\right) - \varphi \quad (4)$$

where the quantity ψ is related to the drag forces exerted by the liquid on the bubble and is defined as:

$$\psi = \left(\frac{3\rho_L}{4\Delta\rho}\right) \left(\frac{q^2\alpha^2}{\pi D_0^2 g}\right) \left(C_d - \frac{16\eta}{3}\right) \quad (5)$$

The quantity φ is defined as:

$$\varphi = \frac{4q^2\rho_L\alpha}{\pi D_0^2} \left[1 - \frac{\alpha}{12} \left(\frac{D_0}{D}\right)^2\right] \quad (6)$$

This latter expression contains terms related to the momentum of the gas.

The application of Equation 4 was accomplished in two steps. The first involved taking data with pure water at various temperatures and evaluation of the unknown factors in Equation 4. The second involved taking data with surfactant solutions and, using the results of step one, to evaluate the apparent or dynamic surface tension.

For step one, data were taken at temperatures of 30°, 50°, 70°, and 90° C. over the frequency range 1000–1900 bubbles per minute in 100 bubbles per minute increments. Over this range φ was negligible when compared to the other terms in Equation 4 and was accordingly discarded. Equation 4 was then written:

$$(1 - \psi) = \frac{\pi D_0 \sigma \left(1 - \frac{D_0}{D}\right)}{\alpha V \Delta \rho g} \quad (7)$$

The quantity $(1 - \psi)$ was correlated with experimental data for pure water using as parameters the dimensionless groups:

$$N_{Re} = \frac{D u \rho_L}{\mu_L} = \frac{\alpha q \rho_L}{\pi D \mu_L} \quad (8)$$

and

$$N_\sigma = \frac{\sigma \rho_L D_0}{\mu_L^2} \quad (9)$$

The group N_σ was used by Hughes and coworkers (2), as a parameter (along with N_{Re}) to correlate measurements of drag coefficients for bubbles. The quantity N_σ is known as the Ohnesorge number and has been used to characterize the breakup of liquid jets (3). It is readily seen that it is equal to the square of the Reynolds number divided by the Weber number ($\rho_L u^2 D_0 / \sigma$).

The data for pure water are shown in Figure 2 as $(1 - \psi)$ vs. N_{Re} at various values of N_σ . Values for $(1 - \psi)$ were calculated using Equation 7. Since the data used were for a pure liquid, the values of σ were the static values which were of course identical with the dynamic values for this special case. From step 2 it was found that the data for determining dynamic surface tension fell within the range: $240 < N_{Re} < 550$; $3.54 < (N_\sigma \times 10^{-5}) < 9.28$. Accordingly, data in these ranges obtained in step 1 were correlated using a multiple, linear regression technique. The equation obtained was

$$(1 - \psi) = 0.6755 N_{Re}^{-.778} N_\sigma^{.272} \quad (10)$$

Equation 10 was used to eliminate $(1 - \psi)$ from Equation 7, the results being:

$$\sigma = \left[\frac{444.9 \rho_L^{.494} \mu_L^{.233}}{D_0^{.728}} \times \frac{D^{2.44}}{f^{.778} (D - D_0)} \right] \quad (11)$$

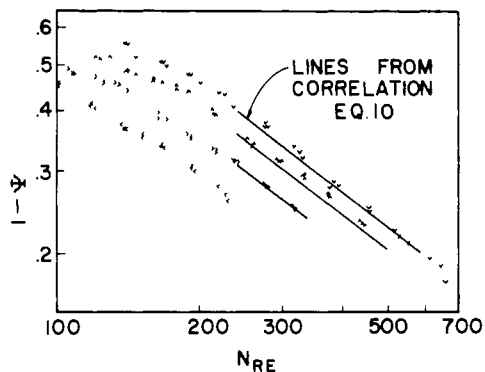


Figure 2. $1 - \psi$ vs. N_{Re} for various N_σ

| | |
|-----------------------------|-------------------------------|
| $< T = 30^\circ \text{ C.}$ | $N_\sigma = 1.76 \times 10^5$ |
| $> T = 50^\circ \text{ C.}$ | $N_\sigma = 3.54 \times 10^5$ |
| $< T = 70^\circ \text{ C.}$ | $N_\sigma = 6.08 \times 10^5$ |
| $< T = 90^\circ \text{ C.}$ | $N_\sigma = 9.27 \times 10^5$ |

Step 2 involved taking bubble volume data with four concentrations of each of eleven surfactants at $T = 90^\circ \text{ C.}$ These data were plotted as V vs. f , and the volumes at $f = 1800$ bubbles/min. arbitrarily used to determine a characteristic dynamic surface tension.

EVALUATION OF α

A Woolensak Fastex camera was used to take four sets of high speed, motion picture photographs. Two of these sequences were with water ($f = 1500$ and 1800 bubbles per minute and $T = 90^\circ$) and two with surfactant solutions ($f = 1500$ and 1800 and $T = 90^\circ$). By projecting the resulting film strips frame by frame, it was possible to compare actual growth rate and final volume to the values determined assuming the bubble contained only dry air. This procedure yielded a value: $\alpha = 2.1$ with a standard deviation of 0.15. On this basis α was assumed constant for the conditions investigated.

STATIC SURFACE TENSION

To provide a comparison, the static surface tension, at temperatures ranging from room temperature to 100° C. , was measured with a duNouy Tensiometer for the eleven surfactants under consideration. The solution was contained in a 250 ml. boiling flask. It was heated with an electric mantle, controlled by a small Variac. Temperatures were measured with a copper-constantan thermocouple contained in a glass well. By careful adjustment of the Variac, it was possible to maintain the solution at constant temperature for sufficient time to read the Tensiometer. At the higher temperature determinations, it was necessary to adjust the Tensiometer between readings to compensate for water which had condensed on the Tensiometer ring stirrup and arm.

RESULTS

Eleven surfactants (see Table I) were considered in this work. The results are plotted as observed dynamic surface tension at $f = 1800$ bubbles/min. and $T = 90^\circ \text{ C.}$, denoted by σ_d , and as measured static surface tension at $T = 100^\circ \text{ C.}$, denoted by σ_{100} , vs. concentration. The data for the Tween series are shown on Figure 3; for the Hyonic series on Figure 4; for the Aerosol series on Figure 5.

The analysis of these results reveals that the trends exhibited are as would be expected. In all cases, σ_d , is

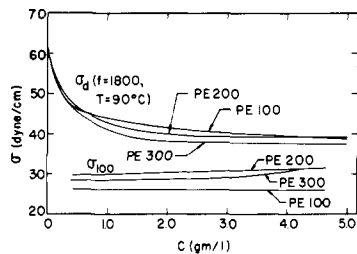


Figure 3. Surface tension vs. concentration for Tween 20, 40, 60, and 80

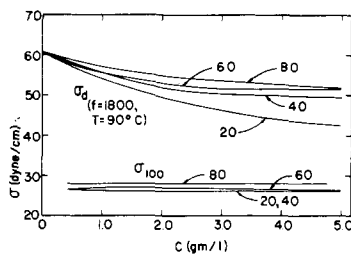


Figure 4. Surface tension vs. concentration for Hyonic PE100, PE200, and PE300

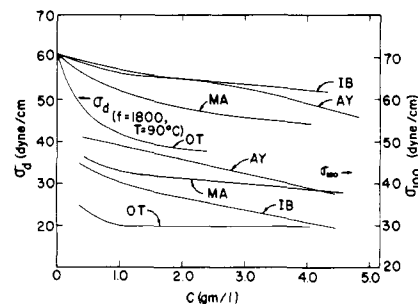


Figure 5. Surface tension vs. concentration for Aerosol IB, AY, MA, and OT

Table I. Properties of Surfactants

| Trade Name | Chemical Name | Mol. Wt. | Sp. Gr. | Manufacturer |
|---------------|---|----------|---------|---------------------------|
| Aerosoll AY | Diamyl Sodium Sulfosuccinate | 360 | ... | American Cyanamid Co. |
| Aerosoll IB | Diisobutyl Sodium Sulfosuccinate | 332 | ... | American Cyanamid Co. |
| Aerosol MA | Dihexyl Sodium Sulfosuccinate | 388 | ... | American Cyanamid Co. |
| Aerosol OT | Diocetyl Sodium Sulfosuccinate | 445 | ... | American Cyanamid Co. |
| Tween 20 | Polyethylene Sorbitan Monolaurate | 1226 | 1.10 | Atlas Chemical Industries |
| Tween 40 | Polyethylene Sorbitan Monopalmitate | 1282 | 1.08 | Atlas Chemical Industries |
| Tween 60 | Polyethylene Sorbitan Monostearate | 1310 | 1.10 | Atlas Chemical Industries |
| Tween 80 | Polyethylene Sorbitan Monooleate | 1308 | 1.08 | Atlas Chemical Industries |
| Hyonic PE-100 | Polyethylene (10) Octyl Phenol Condensate | 536 | 1.078 | Nopco Chemical Co. |
| Hyonic PE-200 | Polyethylene (20) Octyl Phenol Condensate | 856 | 1.117 | Nopco Chemical Co. |
| Hyonic PE-300 | Polyethylene (30) Octyl Phenol Condensate | 1176 | 1.159 | Nopco Chemical Co. |

shown to be less than the surface tension for pure water but greater than the corresponding static value and is a smoothly decreasing function of concentration. In the dynamic situation the effective surface concentration is somewhat less than the equilibrium surface concentration for the indicated bulk concentration. Accordingly, it is to be expected that the dynamic surface tension will be higher than the corresponding static value.

The effect of molecular weight is not as easily explained. If the fractional approach to equilibrium

$$\frac{\sigma_{H_2O} - \sigma_d}{\sigma_{H_2O} - \sigma_{100}}$$

is used as a characteristic parameter, it can be shown that this roughly proportional to molecular weight with the Hyonic and Aerosol series but that the opposite effect is observed with the Tween series. Based solely upon diffusion of the surfactant molecule to the newly formed surface, response of the Tween series might be expected. However, the rate of orientation at the surface is also effective in establishing a dynamic value of surface tension and could perhaps be used to explain the results observed with the Hyonic and Aerosol series.

Since this technique was used to obtain a characterization of the dynamic surface tension in boiling, the effects of temperature and bubble frequency were not investigated in detail.

ACKNOWLEDGMENT

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NOMENCLATURE

- C_d = drag coefficient
- D = diameter of sphere of volume equivalent to bubble (cm.)
- D_o = diameter of orifice (cm.)
- f = bubble frequency (min.⁻¹)
- ΔP = pressure in gas buret (mm. of Hg)
- q = volumetric gas flow rate at T and P at orifice (cm.³/sec.)
- q' = volumetric gas flow rate at T and P of gas buret (cm.³/sec.)
- T = temperature (°C.)
- u = bubble velocity (cm./sec.)
- V = volume of air in bubble (cm.³)
- ψ = defined in Equation 5
- φ = defined in Equation 6
- α = (volume of bubble)/(volume of air in bubble)
- η = that fraction of the displaced mass of liquid which acts as an acceleration drag force
- ρ_L = liquid density (gm./cm.³)
- σ_d = dynamic surface tension at $f = 1800$ and $T = 90^\circ\text{C}$. (dynes/cm.)
- σ_{H_2O} = static surface tension for pure water at $T = 90^\circ\text{C}$. (dynes/cm.)
- σ_{100} = static surface tension at $T = 100^\circ\text{C}$. (dynes/cm.)
- μ_L = liquid viscosity (gm./cm.sec.)

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