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A REVIEW OF SURFACE TENSION MEASURING TECHNIQUES, SURFACTANTS, AND THEIR IMPLICATIONS FOR OXYGEN TRANSFER IN WASTEWATER TREATMENT PLANTS

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ABSTRACT

Dynamic surface tension measuring techniques are reviewed and compared. Dynamic surface tension measurements of various solutions are also presented. From this review the maximum bubble pressure method appears to be the most promising technique of measuring time-dependent surface tension of wastewater solutions. A review of the possible significance of dynamic surface tension on oxygen transfer is also presented.

INTRODUCTION

Surface tension is a measure of the free energy of the surface per unit area. It can be thought of as the work required to expand the surface by unit area. Surface tension of pure liquids, which is a constant value, is measured by techniques now classified as static surface measurement.

Surfactants are substances which alter the surface properties of liquids, even when present in small quantities. Composed of two fractions, a lyophilic group and a lyophobic group, surfactants migrate to the surface, resulting in the lyophilic portion lying within the solution and the lyophobic group orienting itself away from the solution. This orientation of the surfactant reduces the free energy of the surface, thus decreasing surface tension and increasing surface viscosity. Diffusion of surfactants to the surface continues until an equilibrium is established. The transient period when surfactants diffuse to the surface is the basis for dynamic surface tension. Dynamic surface tension measurement techniques are similar to static techniques, differing primarily in the time element.

A consequence of surface tension reduction, especially in aerated wastewater treatment systems, is the production of foam. Although foams often incur no additional treatment costs, they have an unsightly appearance and can result in nuisance residues. Not all surfactants, when used in the same concentrations, produce the same level of foam or have the same persistence to foam. The mechanisms for foam stability are currently under investigation.

Another effect of surfactants in wastewater treatment plants is on oxygen transfer. There is no general consensus as to the actual effect surface tension has on oxygen transfer: some researchers indicate a decrease, others observe an increase, while others see no change. This discrepancy in part results because of differences in aeration devices, but may also be due to the relationship between dynamic surface tension and bubble hydrodynamics.

It is the purpose of this paper to begin preliminary investigation into the relationship between oxygen transfer and dynamic surface tension. The first section of this paper discusses the various surface tension measuring methods, both static and dynamic. The second section addresses the topic of surfactants and surface tension measurements. A related topic also discussed here is foam stability. The last section discusses the relationship between dynamic surface tension and oxygen transfer.

SURFACE TENSION MEASUREMENTS

Surface tension measuring techniques can be categorized into either one of two classes. The first class is static surface tension measurements. Pure liquids are measured with these devices since surface tension values are constant. The second class is dynamic surface tension measurements; many of these are modifications of the static models such as the maximum bubble pressure method and the drop methods. Surfactant solutions should be measured by dynamic methods since surface tension is a function of time, especially during the initial surface ages when a sharp decrease in surface tension is usually observed. The surface tension values approach the static value when surface concentration of surfactants approaches equilibrium.

Before presenting a review of the various methods of surface tension measuring techniques and theories, a distinction must be made between surface age and time. Surface age as defined by various researchers refers to the length of time from surface formation to some specified time (usually until a measurement is taken). Time, in general, refers to the marking of period intervals; surface time is not necessarily measured from the start of surface formation. For example, in the maximum bubble method, surface age is the time interval from the start of the surface formation to the point where the radius of the bubble equal the capillary radius. The time or surface time is the time interval between successive bubble detachments. As defined, surface time is longer than surface age.

Ring Method

The ring method, more formally known as the Lecomte du Nouy ring method (du Nouy, 1918, 1919), is the technique most often used by researchers for static surface tension measurement. The advantage of this method is that the surface tension can be determined directly from the force required to pull the ring from a liquid. There is no need to calibrate the method with other methods or known solutions (Freud & Freud, 1930). Surface tension for the du Nouy method is the mechanical force necessary to lift a platinum ring of known wire radius (R_W) and ring radius (R_R) from the solution surface. The equation describing this process is

$$\gamma = \frac{PF}{4\pi R_R} \tag{1}$$

γ = surface tension
P = force or pull necessary to detach ring from solution surface
V = volume of solution displaced by the pull of the ring
F = Harkins-Jordan correction factor = $f(R_R/R_w, R_R^3/V)$

Harkins and Jordan (1930) investigated the theory behind the ring method to develop tables of empirically-determined correction factors for 16 rings with characteristics: $0.4 \leq R_R \leq 0.8$cm, $0.009 \leq R_W \leq 0.05$cm, and $13.9 \leq R_R/R_W \leq 78.3$. In addition, they presented possible sources of error associated with the ring method, summarized as follows:

1. The plane of the ring must be horizontal to the liquid surface. The associated error is proportional to the square of the angle of tip when the angle is small. This is a necessary condition of the ring method.

2. The diameter of the vessel holding the solution should be greater than 8 cm.

3. The ring should lie in a plane.

Huh & Mason (1975), presenting a rigorous theory of ring tensiometry, concluded that the ring method produced excellent results for surface tension measurement using the Harkins-Jordan correction factors. Their correction factors, however, were consistently higher than those of Harkins and Jordan. The authors attributed this difference to the use of too small measuring vessels by the latter.

Although this method was not designed for dynamic surface tension measurement, application to surfactant solutions has been studied. Lunkenheimer & Wante (1981) investigated the use of the ring method in surfactant surface tension measurements and found, like Huh and Mason, that if the diameter of the vessel holding the solution was too small, errors due to straining can be appreciable. In addition, they found that the maximum pull was dependent on the height between the upper edge of the wetted-wall vessel holding the solution to the solution level for hydrophobic-walled vessels. No dependence was found for hydrophilic-walled vessels, indicating that the surface layer was connected to a layer of surfactant solution on the wetted-wall. They also observed the velocity of the ring lift affected results; faster ring pulls resulted in higher P's.

The equilibrium surface tension values for surfactant solutions obtained by dynamic surface tension measurements are often checked against surface tension values obtained by static measurements. Caskey & Barlage (1971), Burcik (1950) and Vijayan & Ponter (1972) used the ring method while Thomas & Hall (1975) and Kloubek (1975) used the Wilhelmy Plate as methods to verify the equilibrium surface tension value.

Hommelen (1959) found that evaporation, a problem in all liquid surfaces, affected the surface tension value. In general, evaporation produced an initial increase in surface tension for surfactant solutions, reached a maximum, then decreased. Decyl alcohol solutions exhibited extreme behavior by experiencing continuous surface tension increases up to 15 hours.

Hommelen noted the use of static measurements techniques necessitates the attainment of equilibrium concentration of surfactant solutions. It is difficult to know when equilibrium is attained. As seen from Table 1, time to equilibrium varies by surfactant concentrations and type.

TABLE 1: Time to Reach Equilibrium Surface Tension for Various Surfactant Solutions

SUBSTANCE	TIME	REFERENCE
normal nonyl alcohol	10 min	Hommelen (1959)
normal decyl alcohol	60 min	
capric acid	30 min	
dodecyltrimethyl ammonium chloride	<60 min	Caskey & Barlage (1971)
hexadecyltrimethyl ammonium chloride	"	
dodecyl sodium sulfate	"	
hexadecyl sodium sulfate	"	
heptyl and hexyl alcohols	0.01 sec	Defay & Hommelen (1959b)
normal octyl, branched nonyl alcohols	0.015 sec	
3,5,5 trimethyl hexanol	0.015 sec	
0.01M azelaic acid	>15 hours	
0.05M adipic acid	0.01 sec	

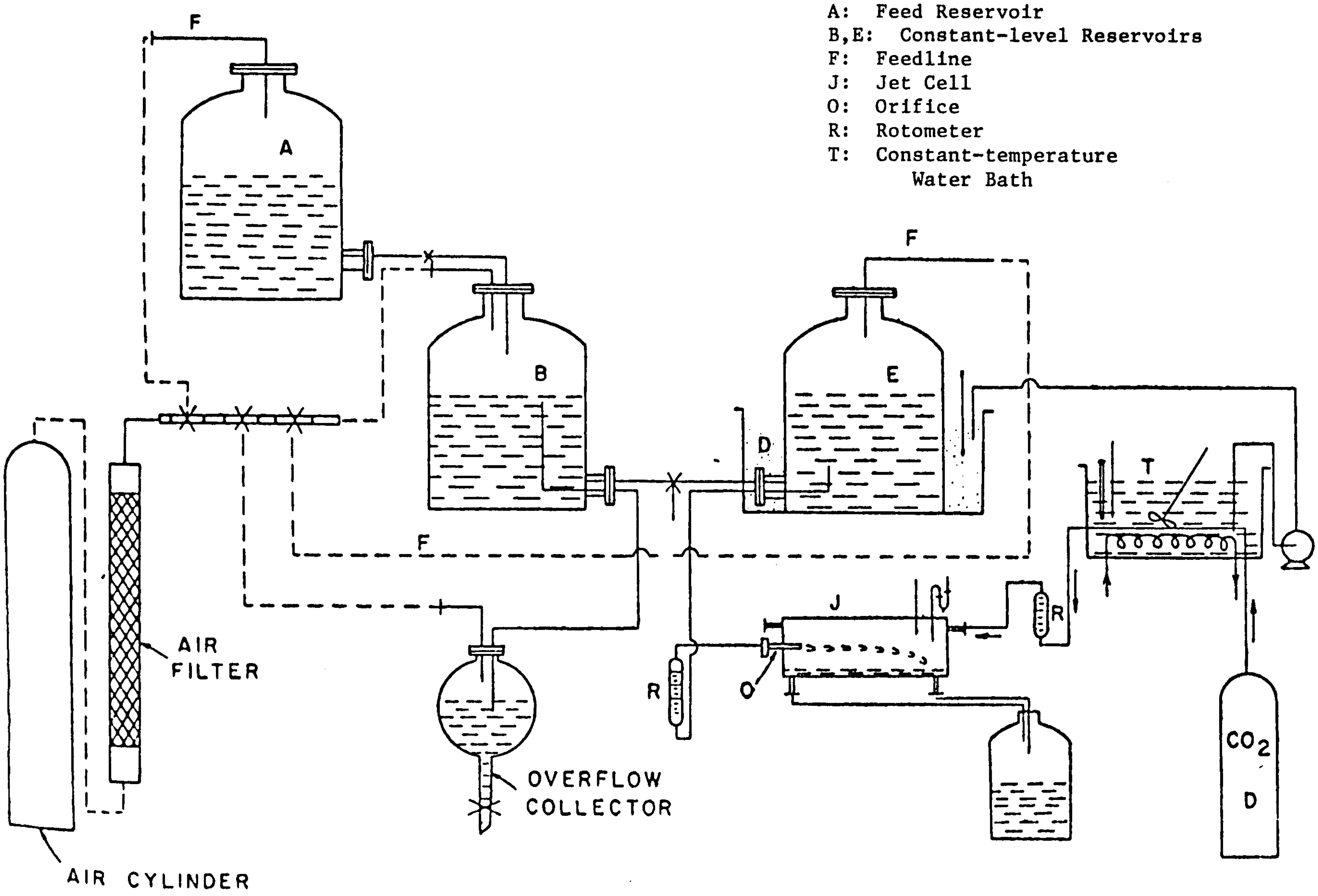
Oscillating Jet Method

The oscillating jet phenomena is the result of pressurized liquid that is forced through an elliptical orifice which produces a jet with properties of standing waves. The oscillating crests and troughs are the result of surface tension forces in the liquid. Bohr (1909) presented the theory and relationship between surface tension and measurable physical properties such as the flow rate of the liquid, wavelength and major and minor axes radii.

Wavelengths are frequently measured by passing parallel light waves perpendicular to the jet stream. Acting as a converging lens, each wave will project a pinpoint light onto a photographic plate situated at the focal length. As the surface tension of the liquid jet changes because of surfactant diffusion to the air/liquid interface, each succeeding wave will have longer wavelength; i.e., will have lower surface tension values. It is obvious that flow rate of the jet will determine the surface age of each wave.

Vijayan & Ponter's (1972) schematic diagram for the oscillating jet is presented in Figure 1. Reservoirs B and E were maintained at constant levels by releases from feed reservoir A, the overflow collector and feedline F. Air pressure and valves regulated the constant-flow oscillating jet. Carbon dioxide gas and reservoir E were kept isothermal through water bath T. Jet flow rates were measured by noting the volume of the jet flow collected in the unmarked flask at various time intervals.

The schematic for the measurement of the jet characteristics via optical properties in shown in Figure 2. Parallel light beams produced by system A-B-C-D were intercepted by the oscillating jet. The light beam translated to



A: Feed Reservoir
B,E: Constant-level Reservoirs
F: Feedline
J: Jet Cell
O: Orifice
R: Rotometer
T: Constant-temperature Water Bath

Fig. 1: Oscillating Jet Experimental Set-up (Vijayan & Ponter, 1972)

A LIGHT SOURCE
B LENS
C PIN-HOLE
D LENS

E SCREEN
F OSCILLATING JET
G PHOTOGRAPHIC PLATE

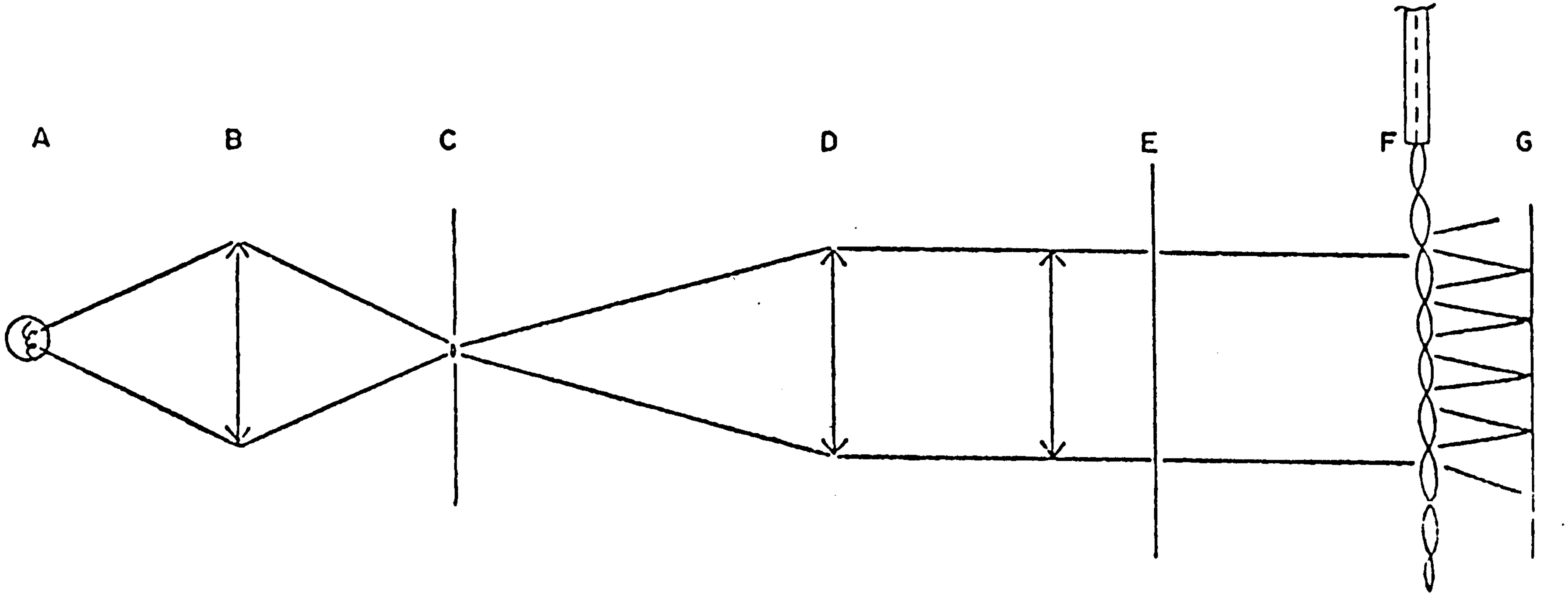


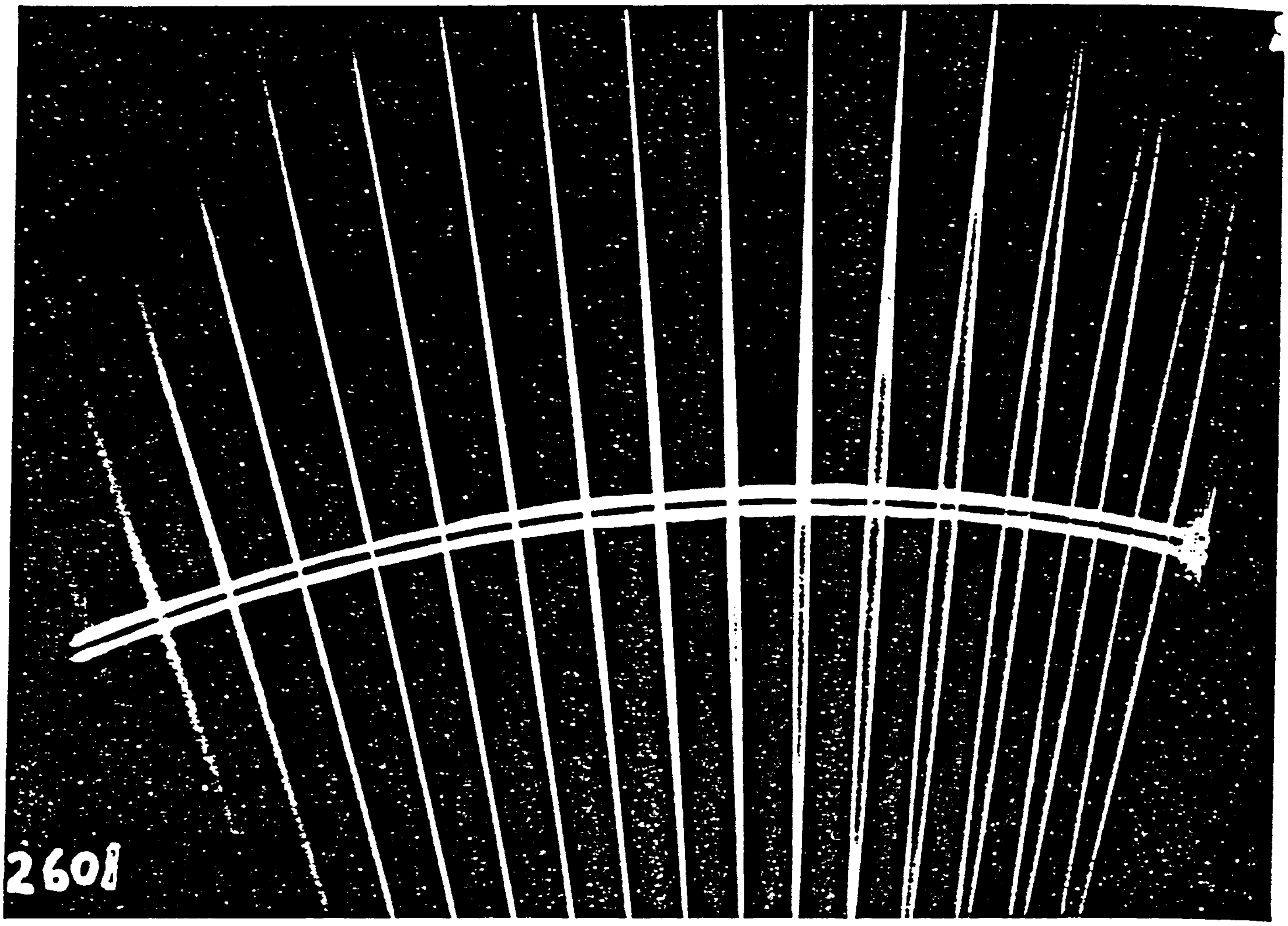
Fig. 2: Optics for Wavelength Measurement (Vijayan & Ponter, 1972)

pinpoints which were recorded on photographic plates. Wavelengths, the distance between each node, were measured directly from the photographic plate using a measuring comparator.

Thomas & Potter's (1975) apparatus for low pressure (1-3 kN/m) measurements is shown in Figure 3. Feed reservoir R was controlled by air flow through needle valve V. A steady rate of 1 drop/sec was allowed to flow through E. This set-up, like the previous one, relied on the system of reservoirs to reduce vibrational interferences. The wavelength was measured from images on photographic plates (see Figure 4) using a Beck microscope with a reading of 2μm. Figure 4) using a Beck microscope with a reading of Amplitude measurements were taken from the camera angle directly above the jet. A calibrated wire gauge mounted above the stream allowed for the direct calculation of distances.

Caskey & Barlage (1971) used a vertical oscillating jet and directly measured the wavelength characteristics with a Gaertner two-coordinate cathetometer. Instead of the usual drawn glass tubing for the orifice, they constructed the orifice from 2.0 mil Mylar film coated on both sides with paraffin. The Mylar film was attached to a Parker tubing nut to form the diaphragm orifice.

An advantage of the oscillating jet method is that surface tension at surface ages from as early as 0.001 sec, can be measured. This ability to calculate surface tension at such early ages is probably the key to resolving the question of the existence of dynamic surface tension for pure liquids. Pure water exhibited dynamic surface tension values for surface ages less than 0.005 sec after which the values remained constant (Thomas & Potter, 1975).



Images from initial 16 waves on a water jet from orifice tube L1 ($f = 2.659$ cm³/sec).

Fig. 3: Images of Waves on Photographic Plate
(Thomas & Potter, 1975)

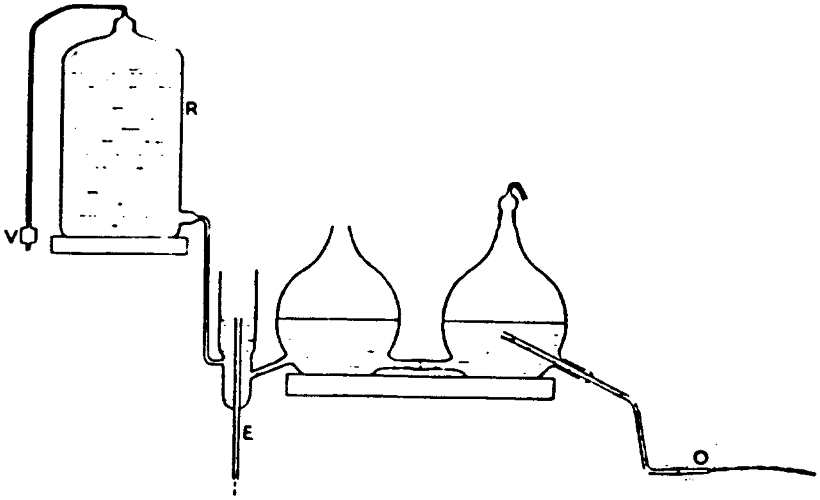


Fig. 4: Oscillating Jet Set-up (Thomas & Potter, 1975)

Caskey & Barlage (1970), also using the oscillating jet, claimed the surface tension values of pure water remained unchanged with time for the surface ages of 0.004 to 0.240 sec — the range of their investigation. Clearly the range of surface ages determines the answer to the question.

The main advantage of the oscillating jet method is the accuracy with which the surface age can be determined. Whereas the surface age from drop techniques are often unknown because of the failure to recognize the moment of surface formation, surface age in the oscillating jet begins at the moment of departure from the orifice. Exact flow measurements will yield a precise estimate of the velocity of the jet. The velocity at the center and the velocity at the edge of the stream, however, are not the same. Most researchers neglect this small difference although Jobert & Leblond (1979) argue for the inclusion of surface velocity profiles along the jet. They state the oscillating jet method is unsuitable for determining the dynamic surface tension of surfactant solutions if the surface velocity profile is not included in the calculations.

Kochurova _et_ _al_. (1974) have included this effect in their experiments by correcting the mean lifetime of the waves using the general Bohr equation as follows:

$$\gamma = \frac{4(\rho_1 + \rho_2)f^2(1 + \frac{37}{24}(\frac{b}{r})^2)K}{6r\lambda^2 + 10\pi^2 r^3} \tag{2}$$

$$K = 1 + 2\left(\frac{\eta\lambda}{\pi\rho_1 c r^2}\right)^{3/2} + 3\left(\frac{\eta\lambda}{\pi\rho_1 c r^2}\right)^2 + \cdots \tag{3}$$

$$\frac{b}{r} = \frac{r_{max} - r_{min}}{r_{max} + r_{min}} \qquad r = \frac{r_{max} + r_{min}}{2}\left(1 + \frac{1}{6}\left(\frac{b}{r}\right)^2\right) \tag{4}$$

where:

ρ_1 = density of the liquid

ρ_2 = density of the air

f = volumetric flow rate

c = axial velocity = $\frac{f}{\pi r^2}$

r_{max} = wave radius at antinode

r_{min} = wave radius at node

η = liquid viscosity

λ = wavelength

This equation is often reduced to

$$\gamma = \frac{4\rho_1 f^2\left(1 + \frac{37}{24}\left(\frac{b}{r}\right)^2\right)}{6r\lambda^2 + 10\pi^2 r^3} \tag{5}$$

since $\rho_1 \gg \rho_2$, $K \simeq 1$ and $r = \frac{r_{max} + r_{min}}{2}$.

Burcik (1950) used an even simpler expression relating surface tension to measurable properties.

$$\gamma = K\,\rho_1\left(\frac{K}{\lambda}\right)^2 \tag{6}$$

In this expression K is a constant which is a function of orifice size and shape. Calibration of K was accomplished with pure water under the assumption that the surface tension of water was static. This assumption was valid since the surface ages were greater than 0.010 sec. He cited the linearity in the rate of flow versus wavelength as justification for the departure from the more complex equation.

As expected from the Bohr equation, the effect of the orifice configuration and orientation have some significance on the resulting values of surface tension. Thomas & Potter (1975) working on both aspects, concluded the extension of the Bohr equation for vertically oriented jets was not valid for horizontal jets. They also developed a relative method for determining the dynamic surface tensions of surfactant solutions by the application of correction factors which were determined by comparison of the surface tension values of water determined from the same orifice and orifice orientation. This eliminated the dependence on capillary orifices. Defay & Hommelen (1958) also addressed the problem of orifice dependence and defined a criteria whereby careful orifice selection eliminated the dependence. In the quest for capillary orifices which met their criteria, of the 50 capillaries made, only 7 were acceptable.

In addition to the disadvantage of orifice selection and dependence, the cost of equipment can be prohibitive for this method. The nature of the parameters necessitates measurement with sophisticated equipment because of the high degree of accuracy required in measuring wavelengths and jet radii. This accuracy results in high equipment costs.

Drop Methods

The basic premise of the drop method is that surface tension can be calculated from physical drop characteristics as it forms at the end of a capillary tip of known external radius. The generic label of "drop methods" encompasses techniques identified by the physical quantity measured: pendant drop (shape), drop-weight, and drop-volume. Although these methods are interrelated, the drop-volume is preferred because of the ease in measuring.

One design (Tornberg, 1977) of the drop-volume measuring apparatus is shown in Figure 5. The drop forms at the base of the brass tip (4) when the piston (6) forced liquid through the capillary. The descending rate of the piston is governed by the rotation of the screw (8) which, in turn, is controlled by a step motor (10). The step motor is connected to an oscillator and the generated pulses are recorded. The volume of liquid released by each pulse is known, therefore the pendant drop volume is also known. The rate of drop formation is then controlled by the pulsing rate of the oscillator. The drops form in saturated liquid vapor in the glass box (3). To prevent liquid from creeping up the outside of the brass tip, a Teflon ring (5) surrounds the tip. The photocell (2) detects the detachment of the drop.

The pendant drop method relies on the hanging drop shape to determine the parameter values necessary to compute surface tension. As expected, this technique is seldom used because of the high cost of equipment necessary to accurately measure these values. Pierson & Whitaker (1974) investigated the shape of the pendant drop to find the drop volume was always less than the pendant drop volume. The stability of the hanging drop was found to be dependent only on its shape. The neutral stability equation was identified as

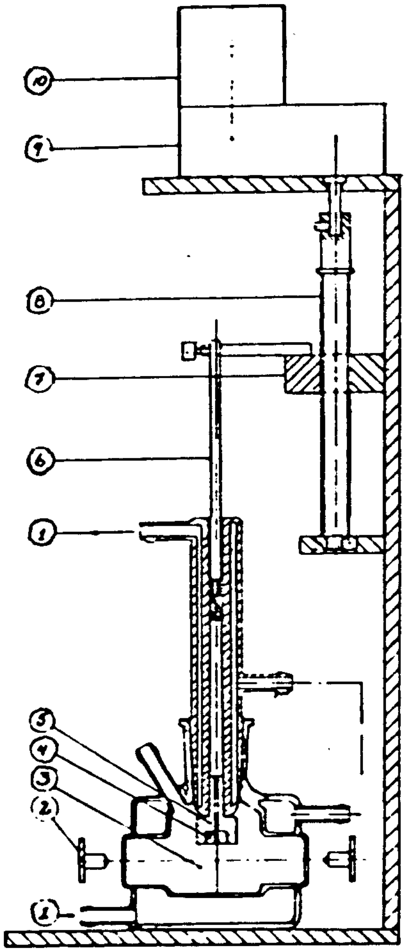
$$\gamma = \frac{\Delta\rho g r_o^2}{f(V/r_o^3)} \tag{7}$$

where:

V = volume of pendant drop

g = gravitational constant

$\Delta\rho$ = density difference between liquid and gaseous mediums



1: Water Jacket
2: Photocell
3: Glass Box
4: Brass Tip
5: Teflon Ring
6: Piston
7: Block
8: Screw
9: Gearbox
10: Step Motor

Fig. 5. Drop-Volume Apparatus (Tornberg, 1977)

r_o = radius of the capillary tip

$f(V/r_o^3)$ = functional relationship dependent on V/r_o^3

The unstable region indicated the falling drop.

The drop-weight and drop-volume processes are similar. The equation for surface tension calculations are:

$$\text{drop weight} \qquad \gamma = \frac{Mg}{2\pi r_o f(r/a)} \tag{8}$$

$$\text{drop volume} \qquad \gamma = \frac{V\Delta\rho g}{2\pi r_o f(r/a)} \tag{9}$$

where

$a = \frac{2\gamma}{\Delta\rho g})^{1/2}$ is a capillary constant.

The value $f(r/a)$ is called the Harkins and Brown (1916) correction factor. The surface tension value appears once in the surface tension calculation and once in the capillary constant, resulting in an implicit equation, which must, therefore, be solved by a series of approximations. A new factor $\varphi(r/V^{1/3})$, was also derived by Harkins and Brown (1916). Wilkinson (1972) developed a fourth-order polynomial relationship between r/a and $r/V^{1/3}$ for these equivalent correction factors for $r/V^{1/3} < 1.20$. He recommended the use of $\varphi(r/V^{1/3})$ because of the smoothing of the correction factors.

As seen from the above equations, the only difference between the drop-volume and the drop-weight methods lies in the selection of the volume or weight measurement. The drop-weight has been extensively used because of the speed and accuracy in which measurements can be made. However, with the increased accuracy of microburets, it has become equally advantageous to use the drop-volume technique.

Kloubek _et_ _al_. (1976) and Pierson & Whitaker (1976) confirmed that the lower area of the capillary tip affected the size and shape of the drop mass. The inner diameter of the capillary controlled the flow rate of the solution but not the drop mass for a given time period. An important result of Kloubek _et_ _al_. was that the Harkins and Brown correction factors were not applicable for use with dynamic measurements.

A major problem of drop methods is the determination of surface age. The surface age is generally taken to be the time interval from drop formation to drop detachment. Surface tension lowering due to surfactant diffusion to the surface results in drop detachment. Surface age is a function of the measuring technique of the experimenter who must subjectively define the start of the surface. In addition, Hommelen (1959) found that subsequent drops were contaminated with residues from previous drops, and that drops with long surface ages were subject to evaporation effects.

Maximum Bubble Pressure Method

The maximum bubble pressure method is based on the maximum pressure in a capillary or a maximum pressure difference between two capillaries of different radii necessary to produce and detach a bubble from the capillary tip immersed in test solution.

One of the first maximum bubble pressure measuring apparatus for surface tension (see Figure 6) is attributed to Sugden (1922). Mercury was held in the flask to the extreme right. Two capillaries of different radii were sealed onto the test tube containing the liquid by a rubber stopper. The capillaries, open to the atmosphere, could be open or closed to air flow by rubber stoppers. By releasing the mercury from the flask into the beaker (a pressure drop was created in the system as noted by the manometer) air was drawn into the capillary to form the bubble. Capillary radius and the mercury flow rate controlled bubble formation rate.

Bendure's (1971) schematic diagram for his work with the maximum bubble pressure method is shown in Figure 7. Argon gas (1) flowed through the inverted test tube (3) filled with water which released water that flowed through a rotameter and was collected in the test tube (5). The increase in pressure in test tube (5) resulted in the formation of the bubble in the beaker (6). The bubble pressure was sensed by a Bourdon tube pressure gauge capable of pressure differentials of 300 torr (8). The 100-ohm resistor (9) converted the current output to voltage that was recorded on the strip chart (10).

Figure 8 shows Razouk & Walmsley's (1974) capillary unit, conceptually similar to Sugden's two-capillary unit, except the design is more sophisticated. The regulated, vapor-saturated nitrogen gas flowed into the capillary system at constant temperature. The gas flowed into either of the submerged wide- or narrow-tube capillaries at a constant rate (2-4 bubbles/min). A differential pressure transducer, diaphragm-resistive unbonded-strain gauge type, across the gas inlet was connected to a bridge supply. Signals were recorded on a strip chart. Standard pressures were used to calibrate the transducer, which resulted in a linear relationship between pressure difference and output signal.

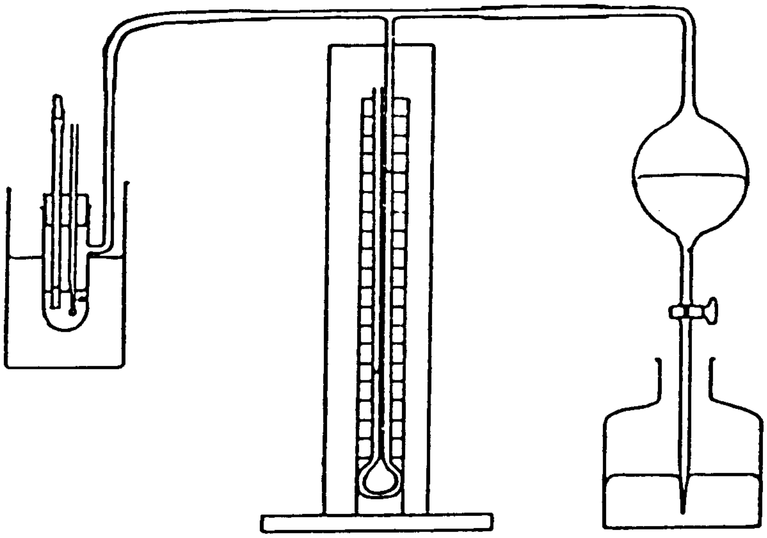
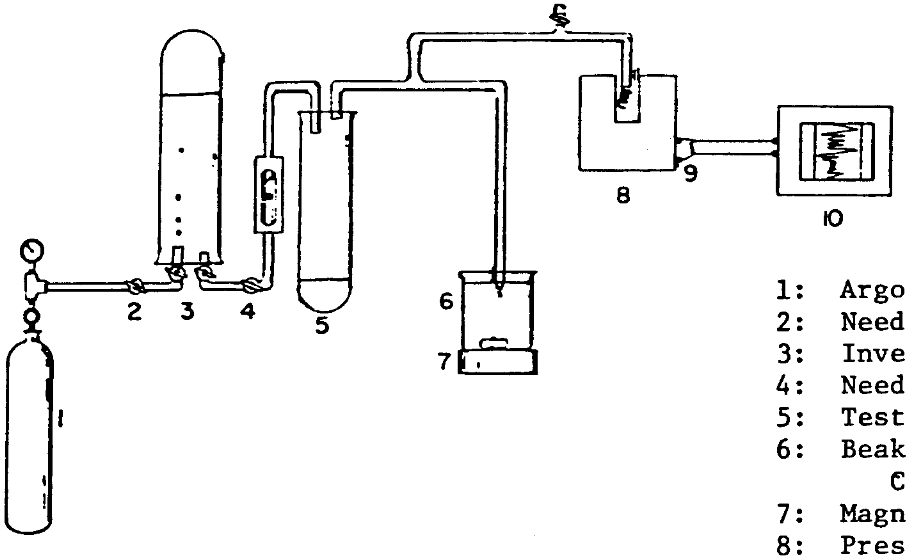


Fig. 6. **Maximum Bubble Pressure Experimental Set-up (Sugden, 1922)**



1: Argon Gas
2: Needle Valve
3: Inverted Test Tube
4: Needle Valve and Rotometer
5: Test Tube
6: Beaker with submerged Capillary Tip
7: Magnetic Stirrer and bar
8: Pressure Gauge
9: Resistor
10: Strip Chart

Fig. 7. Maximum Bubble Pressure Experimental Set-up (Bendure, 1971)

Based on two capillaries, Sugden (1922) outlined the equation for surface tension as:

$$\gamma = \frac{H_g \Delta\rho}{2(\frac{1}{X_1} - \frac{1}{X_2})} \qquad (10)$$

where:

H = height difference (pressure) between capillaries of different radii

$$= h_1 - h_2 = a^2(\frac{1}{X_1} - \frac{1}{X_2}) \qquad (11)$$

a^2 = specific cohesion

In this equation, approximation of X_i $(i = 1,2)$ must be made so a^2 can be calculated by $X_i = a^2/h_i$. The usual first approximation is $X_i = r_i$, where r_i is the capillary radius. r_i/a is then matched to some X_i/r found in published tables. For the new values of X_i/r_i a new value of X_i can be determined. A constant value of a^2 is taken to be the stopping criteria.

In further work on surface tension, Sugden (1924) found gD/P to be nearly proportional to a^2, X_i changes little between liquids, and r_1 to be small, so the equation can be simplified to

$$\gamma = AP(1 + 0.69r_2 \frac{gD}{P}) \qquad (12)$$

where A is an apparatus constant and D is fluid density. The results of surface tension using both equations were in fair agreement.

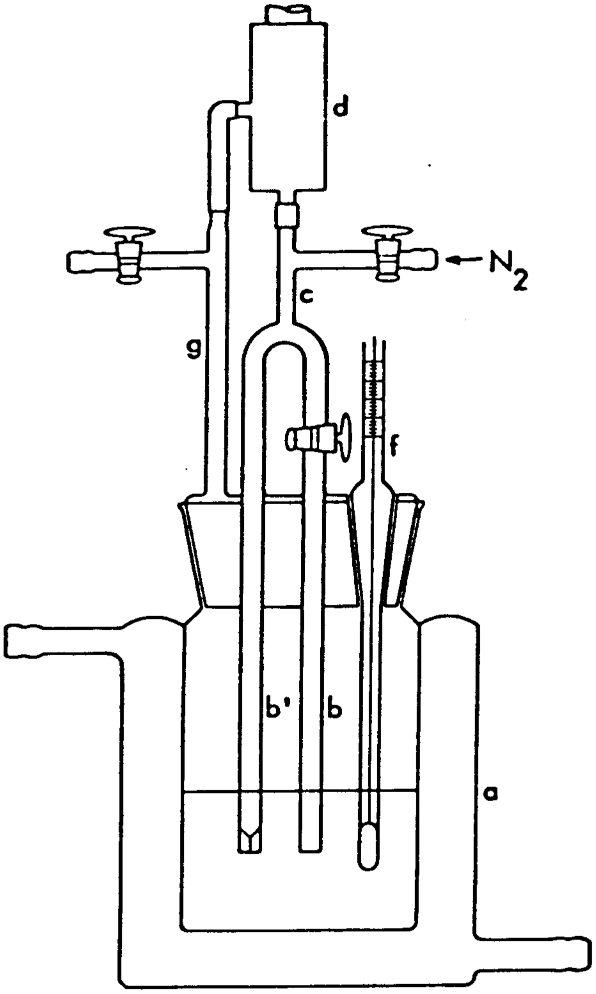


Fig. 8. Two Capillary Unit Design
(Razouk & Walmsley, 1974)

Bendure (1971) used the equation

$$\gamma = \frac{rPf}{2} \tag{13}$$

where

r = capillary radius

P = pressure across bubble interface

f = correction factor where $f = f(r/a)$

a = capillary constant = $(\frac{2\gamma}{\Delta\rho g})^{1/2}$

A fifth-order power series equation was developed by least squares regression for tabulated values of Sugden's f. This equation reflects the use of one capillary, and iterations are still necessary for a solution.

Again, the major difference between dynamic and static surface tension measurements is a careful accounting of surface age. In the maximum bubble pressure measuring technique, the time interval between bubble detachments (surface time) is usually defined as a composition of surface age and dead time. Surface age and dead time are defined as :

surface age (T): (effective surface age)	Surface age is the time interval from the start of the fall of the meniscus to the start of the formation of the bubble at the tip of the capillary.
dead time:	Dead time is the time interval from the end of the surface age to bubble detachment (period of rapid bubble growth).

Most of the adsorption process of surfactants to the interface occurs during the surface age. In this period, the surface area remains constant so the calculation of adsorption is fairly easy. During dead time, the rapid bubble growth prohibits adsorption of surfactant on the surface. It is apparent that at low bubbling frequencies dead time is not as important as during high bubbling frequencies when dead time can be a significant part of surface time. Austin <u>et</u> <u>al</u>. (1967) gave the dead time correction to be 31.9 - 0.00042S msec where S is the bubbling frequency. This empirically-determined correction factor is independent of capillary radius for capillaries with heads between 19.7 to 26.4 cm of pure water at the maximum bubbling frequency. The authors believe 10 msec to be the shortest surface time before errors occur.

Another estimation of dead time is given by Fainerman (1979)

$$\tau_d = A \left[\frac{1}{3} \left(\frac{R}{r_o}\right)^3 + \frac{B}{2r_o} \left(\frac{R}{r_o}\right)^2 \right] \tag{14}$$

$$A = \frac{32l\eta}{r_o \Delta P} \qquad B = \frac{2\gamma}{\Delta P} \tag{15}$$

where:

R = detached bubble radius

ΔP = maximum pressure in the bubble

l = length of capillary

η = dynamic viscosity of gas

r_o = capillary radius

A plot of dead time vs. lifetime of the bubble (τ_r) showed that for lifetimes <0.65 sec, $\tau_d \simeq \tau_r$. This is in fair agreement with Kloubek's (1972) dead time values determined from photographing the bubbling sequence, and correlated film speed with bubble formation.

Kloubek (1972) did extensive work in the maximum bubble pressure method. His results show:

1. The volume of the bubble is independent of the capillary tip immersion depth.
2. The diameter of the detached bubble increases linearly with capillary diameter.
3. Capillary orientation affects the bubble separation process.
4. A decrease in bubble volume is experienced with an increase in bubble frequency.
5. There exists a maximum bubbling frequency at which only dead time exists and above which pressure is no longer related to surface tension.

Other Methods

The methods of measuring surface tension described in the preceding sections are the techniques used by most of the researchers in this field. This does not, however, complete the list of techniques used to measure surface tension. The following methods of dynamic surface tension measurement are either new or less frequently used by the researchers.

Kochurova & Rusanov (1981) determined dynamic surface tension values by correlating them to surface potentials. The oscillating jet method was used to determine surface tension with the surface velocity profile correction included in the calculations of surface tension. Surface potential was measured by the dynamic condenser method at 24°C. The equations of dynamic surface tension and surface potential were similar:

$$\text{surface tension} \qquad \Delta\gamma = (\gamma_0 - \gamma_\infty)e^{-t/\tau} \qquad (16)$$

surface potential $$\Delta x = (x_0 - x_\infty)e^{-t/\tau} \tag{17}$$

t = time

τ = relaxation time

where:

subscript 0 : initial value of measured quantity

subscript ∞ : equilibrium value of measured quantity

The relationship discovered between these two qualities was:

$$\Delta\gamma = \alpha|\Delta x| + \beta|\Delta x|^2 + \delta|\Delta x|^3 + \cdots \tag{18}$$

where α, β, δ, are calibrated parameters. This equation was valid when change in oriented dipole number and change in surface potential were small. The authors were able to determine the coefficient values from their data. Their data also revealed equilibrium surface tension for water was reached at 3 msec and as $t \to 0$, γ = 100 dyne/cm for pure water.

A variation of the maximum bubble pressure method was proposed by Suzuki _et al_. (1972). In this version, a bubble of surfactant solution is blown into the air, rather than air being blown into the surfactant solution. The bubble shaped formed in air provided the basis for surface tension calculations.

The falling meniscus method for surface tension measurement is based on the principle that the height of a liquid in a tube is dependent only on the radius of the capillary opening at the meniscus position. A tube is lowered into bulk solution until a meniscus is formed at the small capillary orifice at the top of the tube. The bulk solution is then lowered until a critical height, h_o, marked by the rupture of the meniscus. The relationship to surface tension is:

$$\gamma = \frac{\rho g r}{2} (h_o - \frac{2r}{3}) \tag{19}$$

where:

r = capillary radius

h_o = height of meniscus break above bulk solution

The dynamic surface tension measurement is performed by maintaining a constant h_o, then marking the surface age which is defined by the time interval from the meniscus formation to meniscus rupture. Defay & Hommelen (1959) showed surface contamination, surface extension, and evaporation can significantly affect the value of surface tension. They proposed methods whereby the influence of these effects could be made negligible.

Summary

Clearly the ring method is unsuitable for dynamic surface tension measurements. This method is applicable only when the concentration of surfactants has established equilibrium at the surface. At equilibrium, the ring method can give an absolute value of surface tension.

The disadvantages of the drop methods out-weighs their advantages. The effect of the capillary tip may give unreliable parameter estimates, which will produce poor estimates of surface tension. Evaporation and contamination of the surface are problems for long surface times. In addition, the surface age is difficult to identify. The only advantage of this method is the experimental set-up is simpler than most methods.

The oscillating jet has many advantages. The main attraction is the very early surface ages that can be attained by this method; surface ages of 1 msec have been recorded. This method also gives reasonably accurate values of surface tension even if the jet velocity profile is not included in calculations. Furthermore, the relative method of the oscillating jet eliminates the dependence on the capillary tip. The main disadvantage to this method is the cost of the special equipment required.

The maximum bubble pressure method seems to be the method of choice for the determination of dynamic surface tension. The measuring technique for dead time and surface age been improved, and the method does not suffer from evaporation effects. Although the range of surface ages is much greater than that of the oscillating jet, one of its earliest recorded surface age is only 10 msec. The equipment costs for this method are low.

Tables 2-5 summarize the results of various researchers in the dynamic surface tension field.

Table 2. Dynamic Surface Tension Measurements: Drop Methods

Description	Comments	References
Drop-weight, drop-volume and drop-length methods rely on accurate drop characteristics measurements to determine surface tension. The main disadvantages of these methods are difficulty in determining short surface ages and accounting for the effect of the expanding surface.		
Drop length	Difficult to establish surface ages.	Hommelen (1959)
Drop volume	Pulses generated by an oscillator control drop volume. Used Harkin's & Brown's correction factors.	Tornberg (1977)
	Ward-Tordai equation was not valid for changing surface area. Assumed spherical shape of the drop.	Joos, _et al_. (1981)
Drop Weight	Used one stalagmometer. Corrections of Harkins & Brown were applicable only when drop formation time was long. Each point represented a separate test so the results were reproducible.	Kloubek (1975)
	Used various stalagmometers. $0 \leq t \leq 100$ sec.	Kloubek, _et al_. (1976)
	Drop shape and stability were discussed for $t < 20$ sec.	Pierson, _et al_. (1976)
	Rate at which drop break-up occurred was dependent directly on surface tension, and capillary radius but inversely proportional to fluid density and the square of the viscosity.	

Table 3. Dynamic Surface Tension Measurements: Maximum Bubble Pressure Method

Description	Comments	References
This method is based on the maximum pressure needed to liberate bubbles from a capillary submerged in test solution. Pressure increases are measured as functions of time.		
One capillary stroboscope was used to measure bubble frequencies. Filming techniques were used to determine surface age.	Determined that the limit to maximum bubbling frequency. occurred when time of bubble formation approached dead time. $0.010 \leq t \leq 0.120$ sec.	Austin, *et al*. (1967)
One capillary; used water passing through a rotameter to measure air flow rate.	Most adsorption occurred when surface area was constant. Diffusion-controlled mechanism of mass transfer $t < 100$ sec.	Bendure (1971)
Two capillaries; stroboscope was used to measure bubble frequency.	Volume of the bubble was independent of capillary tip immersion depth. Diameter of the detached bubble increased linearly with increasing capillary diameter. Existence of maximum obtainable bubbling frequency confirmed.	Kloubek (1972)

Table 4. Dynamic Surface Tension Measurements: Oscillating Jet Method

Description	Comments	References
Test solution is forced through an elliptical orifice producing a stream with oscillating wave characteristics. The wavelength and radii (maximum and minimum) of each wave determines surface tension while wave position determines surface age. The main advantage in this method lies in the accuracy in which the surface age can be calculated.		
Light beams were used to find Wave characteristics. Radii measured by calibrated moving rectilinear eyepiece.	Eliminated dependence of capillary orifice on surface tension values by standardizing with solutions of known surface tension and application of correction factors.	Defay, *et al*. (1958)
Two-coordinate cathetometer was used to measure wave characteristics from a photograph. Orifice was constructed of mylar film attached to stainless steel tubing nut. Vertical jet orientation.	Water may wave dynamic surface tensioned for t < 0.006 sec.,	Caskey, *et al*. (1971)
Parallel light beams were used to define waves. Wave characteristics were measured off of photographic negatives by a measuring comparator.	At low surface ages, surface tension was dependent on liquid flow rate. At higher ages it became independent of flow rate. Water exhibited dynamic surface tension behavior. Bohr's equation was applicable for ages t > 0.006 sec.	Vijaya, *et al*. (1972)
Uniform and bell-shaped glass capillary orifices were used. Vertical and horizontal orientations were used.	Surface tension depended on orifice orientation. Evidence of dynamic surface tension for distilled water for t > 0.006 sec. Relative method of determining true surface tension values was proven to be valid.	Thomas, *et al*. (1975)

Table 5. Other Methods

Description	Comments	References
Falling Meniscus		
This method is based on the principle that the height of a liquid in a tube is dependent only on the radius of the tube where the meniscus is situated.		
	Surface age was measured from time of meniscus formation. Pollution and contamination effects were discussed.	Defay, *et al.* (1959)
Surface Potential		
Dynamic surface tension is related to dynamic surface potential.		
	Dynamic surface tension values were affected by evaporation.	Kochurova, *et al.* (1981)

SURFACTANTS

Surfactants are substances that, when present in low concentrations, have the ability to significantly alter the surface properties of the solvent. These compounds are generally composed of lyophobic and/or lyophilic groups. When the lyophobic group lies within the solvent it disrupts the structure of the surface, thus decreasing the free energy of the system, while the lyophilic group prevents the complete expulsion of the surfactant from the solvent.

Of the hundreds of existing surfactants, many have numerous applications. The choice of surfactant for a specific purpose is difficult and the following information can aid in the selection of the surfactant (Rosen, 1978).

1. Characteristic features of commercially available surfactants.
2. Expected interfacial phenomenon involved and the role of the surfactant.
3. Surface chemical properties of various structural types of surfactants.

All surfactants, however, can be categorized by the charge on the surface-active component into: (1) anionic, (2) cationic, (3) nonionic, and (4) zwitterionic (both positive and negative charges).

Surface Tension

Surfactants reduce the amount of work necessary to create unit surface area, i.e., surface tension of a solution is lowered when surfactants are present. The following are a few generalizations regarding surface tension and surfactants, followed by a discussion of surfactants and dynamic surface tension.

1. Higher concentrations of surfactants lower the surface tension in comparison to the pure solvent state. The limiting value of surfactant concentration that produces a surface tension decrease is the critical micelle concentration (Caskey & Barlage, 1971). Furthermore, the steeper decrease in surface tension is evident only at high surfactant concentrations.
2. Using the Wilhelmy plate method, Lange (1965) found that γ is dependent on its prehistory. Compressing the surface once or twice altered the equilibrium value of surface tension.
3. Surface tension decreases with increasing temperatures (Tornberg, 1977). This decrease can be attributed to the higher surface activity at the higher bulk temperatures. At equilibrium γ increased with temperature or remained invariant (Kloubek, 1972b).

Contaminates on the gas/liquid interface can affect the dynamic surface tension measurement. In drop stability analysis, for $t < 200$ sec, surface tension appeared to be constant for an 0.08M hexanoic acid solution (Pierson & Whitaker, 1976). After 200 sec, surface tension increased with time. Slow adsorption of contaminates in the system was postulated for this anomality. Gilanyi _et al_. (1976) attributed the competitive adsorption process of contaminates as the mechanism for prolonged time dependence of surface tension which could not be explained solely by diffusion. They supported the theory that a necessary, but not sufficient, condition for surface purity is an absence of a minima in the γ versus ln (c) curve. Surface purity depends on surface life-time and experimental method.

The effect of electrolytes has been studied by a few researchers. Lauwers & Ruyssen (1964) found the addition of electrolytes (sodium salts: NaCl, Na_2SO_4, Na_2HPO_4, and NaH_2PO_4) decreased surface tension in solutions of β-lactoglobulin. Solutions of Maxonol (0.0003M to 0.003M) exhibited sharp increases in the initial rate of surface tension decrease in 0.027M NaCl solution (Austin _et_ _al_., 1967). The effect of NaCl on surfactant solutions was also dependent on the type of surfactant (Shah _et_ _al_., 1978). Nonionic surfactants seemed to exhibit no change in surface properties. Burcik (1950) explained the decrease in surface tension could be attributed to the charge accumulation in the diffusive layer repelling the approaching surfactant molecules, assuming the surfactants were ionic. This was supported by the experiment in which nonionic surfactants did not exhibit electrolyte effect in surface tension measurements.

Surfactant orientation may also influence dynamic surface tension measurements. When the oscillating jet was used as the measurement technique, a common feature of surfactant solutions appeared to be the contraction of wavelengths for very early surface ages and an extension of wavelength for longer surface ages. For early ages, the surfactant is not allowed the opportunity to orient the hydrophobic group to the outside of the jet. At longer ages the polar orientation becomes established so the hydrophobic group lies outside of the surface, allowing for the surface tension decrease (Thomas & Hall, 1975).

The mechanism of mass transport is of great interest in surfactant study. It appears that there is a general consensus that the diffusion process describes the mass transport of surfactants to the air/liquid interface.

However, controversy arises over the existence of an energy barrier at the surface.

Proponents for the existence of a barrier see it as a subsurface layer between the bulk solution and the surface. The surfactant molecules are instantaneously in thermodynamic equilibrium at the bulk/subsurface interface (a Ward-Tordai assumption). The concentration gradient from the bulk to the surface promotes the diffusion of surfactants to the surface, during which time surface concentration can be related to time by

$$\Gamma = 2C_o \left(\frac{Dt}{\pi}\right)^{1/2} \tag{20}$$

where:

Γ = surface concentration

D = diffusivity

C_o = bulk concentration

As the finite active sites of the surface become occupied, back diffusion occurs from the surface to the bulk. At this time the Ward-Tordai equation (which relates surface concentration to time) governs. Defay & Hommelen (1959) found the low values of calculated γ supported the existence of the barrier.

Suzuki _et_ _al_. (1972) observed for bubbles in air that the surface tension increased with time, reached a maximum, then decreased. In the rising portion, they speculated that the depth of the surface layer decreased with time as the bubble increased in surface area, producing an increase in the surface tension. In the latter region, the subsurface layer became the surface layer, so surface tension decreased by increased mass transport of surfactants to the surface.

Contrasting the observations of Suzuki, et al. (1972), Lange (1965), using the Ward-Tordai and the v. Szyskowski equations, concluded time dependence of surface tension was controlled by diffusion through a diffusive layer whose thickness increased with time. This diffusive layer, therefore, was unaffected by convection from the bulk solution.

On the opposing side, Joos & Rillaerts (1981) proposed the Ward-Tordai equation was not applicable to the expanding surface of the drop methods or bubble methods, and that convection near the surface did occur due to the motion of the expanding surface. Furthermore, the spherical shape of the drop was valid but was an incorrect assumption for the maximum bubble pressure method. For short adsorption times, the equation describing the surface concentration with convection was

$$\Gamma = 2C_o \left(\frac{3Dt}{7\pi} \right)^{1/2} \tag{21}$$

A dilation time was included for the expanding surface yielding:

$$\Gamma = 2C_o \left(\frac{Dt}{\pi(2\alpha+1)} \right)^{1/2} \qquad \theta = \frac{\alpha}{t}\ , \ 0 \leq \alpha \leq 2/3 \tag{22}$$

When $\alpha = 0$ this equation reduced to the first term of the Ward-Tordai equation. Deviation from the spherical shape occurred when $\alpha > 2/3$. This equation tested on Bendure's work resulted in the conclusion that no barrier for diffusion need be postulated.

Bendure (1977) derived equations for short-term and long-term adsorption times based on Langmuir description of adsorption processes. The equation relating dynamic surface tension to time were

long adsorption $$\gamma-\gamma_\infty = \frac{\Gamma^2 RT}{(\pi D)^{1/2} C_o (t)^{1/2}} \tag{23}$$

short adsorption $$\gamma-\gamma_o = C_o 2RT(\frac{D}{\pi})^{1/2} t^{1/2} \tag{24}$$

where:

R = universal gas constant

γ_∞ = equilibrium surface tension

γ_o = surface tension of pure solvent

For long adsorption times, the above equation shows $\gamma-\gamma_\infty$ vs $t^{-1/2}$ and for short adsorption times $\frac{\gamma-\gamma_o}{C_o}$ vs $t^{1/2}$ should be linear. Using estimates of the diffusivity constant found from the limiting cases of both adsorption times, the data using four surfactants (dimethyl decylphosphine oxide, dimethyl dodecylamine oxide, dimethyl dodecylphosphine oxide and n-dodecyl hexaoxyethylene glycol monoether) at various concentrations were plotted both ways. The plots confirmed the "correctness" of the equations and assumptions.

Another manner in which to check the equilibrium surface tension of surfactant solutions has been used by Kloubek (1972b). $\frac{1}{\gamma_\infty-\gamma}$ vs $\frac{1}{t^{1/2}}$ was used in the maximum bubble pressure method with sodium dodecyl sulfate. As $t^{1/2} \rightarrow 0$, equilibrium surface tension should be reached. (γ_o is the surface tension of the pure solvent.) At low concentrations of surfactant (0.00076M and 0.00088M) the curves were non-linear, at higher concentrations the lines were more linear in the surface age range $t < 10$ sec. Extrapolation of the curves by extension of the linear portion of the curves gave better results than the extension of the fitted curve. Kloubek (1975) also used $\frac{1}{\gamma_o - \gamma}$ vs $\frac{1}{t}$ to determine the equilibrium surface tension for results by the drop method. In this instance, although the range of values was wide, the average value agreed well with the static method determination.

Foaming

Foaming is an important aspect of surfactant characteristics since foaming can be a nuisance in aeration basins. Also, foaming is closely related to surface tension. This paper only addresses foam production by gas injection into a liquid phase.

Since foam is composed of gas pockets surrounded by thin films, a study of film properties is necessary before foam can be discussed. The films between bubbles which compose the foam are called the lamellae of the foam. The equation relating the pressure change across these lamellae is described by the Young-Laplace equation:

$$\Delta P = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \tag{25}$$

R_1 and R_2 are the radii of curvature at a point on the lamella. R_1 and R_2 swing in perpendicular planes to the surface and to each other. This equation determines the shape of films formed on wires dipped in surfactant solutions (Bikerman, 1973).

It should be noted that pure solutions do not foam. Gas bubbles beneath the liquid surface rupture upon contact with each other or with the surface because surfactants are unavailable to adsorb to the surface to decrease the surface tension. Lamellae cannot be formed by inelastic surfaces. Film elasticity is a necessary but not a sufficient condition for foaming (Bikerman, 1973).

The effect of gravity on the lamella is to drain the liquid from the film. Thus, the top of the film becomes thinner and the bottom, thicker. It is not the over-all thinning that results in film rupture but a localized thinning in one spot. At a local thin spot, the surface tension is slightly higher than the immediate surrounding area because the amount of surfactants in that spot is less. Mechanical film response to thin spots are known as the Marangoni-Gibbs effect. The Gibbs effect is a change of surface tension with a change in the surface-active solute concentration based on an equilibrium value of surface tension. The Marangoni effect is a change in surface tension with time and is based on an instantaneous surface tension value. These effects are complementary, both describe the same effect. Since a surface tension gradient exists at the thin spot, it results in the movement of liquid from surrounding areas to that spot, leading to the physical restoration of the film. Additionally, the liquid from the surrounding areas bring solute molecules to the spot to reduce surface tension and the spot regains local equilibrium with the surrounding areas. If the draining occurs at a faster rate than the restoring Marangoni-Gibbs effect, the film ruptures (Rosen, 1978).

Foams behave like films. When three or more bubbles meet, the intersection point of all lamellae is called the Plateau border (Bikerman, 1973). Bubbles assume positions as dictated by capillary pressure and surface tension. For three bubbles, the angle formed by the lamellae is 120°; this is proven by the fact that each lamella pulls at the Plateau border by force/unit length of 2γ. These equal forces act in one place balance only if the angles between them are equal, i.e., 120°. The most stable foam structure occurs when three bubbles meet at the Plateau border.

Foam stability has been discussed by several researchers. There is, however, no consensus on a uniform definition of foam stability. Although the Ross-Miles test is the most frequently used. Presented below are various criteria of foam stability. The following stability tests or criteria have been proposed:

1. Pour foam test (also known as the Ross-Miles test). 100 ml of solution is allowed to fall through a height of 70 cm from a separatory funnel into a graduated cylinder. Both the time until total initial foam breakdown and time to break initial foam volume to one-half are taken as measures of foam stability (Burcik, 1950).
2. Single bubble test. The average lifetime of 20 to 30 uniformly-sized small bubbles in CO_2-free water was taken as a measure of foam stability (Burcik, 1950).
3. The minimum volume of solution drained from the foam after a specified length of time (Shah _et al_., 1978).
4. Foam stability was defined as $\theta = G/d$, where G = total volume of the dispersed gas obtained when foam volume (V) and liquid content (L), reached a maximum, $G = V - L$. d = calibrated gas flow rate. θ was dependent only on the physiochemical properties of the the solution (Lauwers & Ruyssen, 1964).
5. The ratio of the initial height of the foam column, H_o, from the Ross-Miles foam test to the height of the foam column after 5 minutes, H_5. K = foam stability = $(H_o/H_5)100$ (Chistyakov _et_ _al_.,

1979).

Maximum shear viscosity corresponded to minimum average drainage rate for the same concentration of sodium dodecyl sulfate (SDS) with decanol (DOH) (Shah <u>et</u> <u>al</u>., 1978). The maximum/minimum was dependent on the K ratio, K = conc SDS/conc DOH, such that the concentration of SDS at which the maximum/minimum occurred increased as K decreased. Results of foam stability on steric acid - steryl alcohol solutions indicated a correspondence between foam stability maximum and tight packing of the molecules. The ratio of concentrations where foam stability was highest occurred with the tighter packing of the molecules at the monolayer interface.

In another experiment, solutions of triethanolamine (TEA) salts of alkyl phosphates and TEA salts of individual mono- and didodecyl phosphates were tested for foaming power. Foam stability, measured by the Ross-Miles test, increased as the concentration of the surfactant increased, but decreased as the number of carbon atoms increased. The equation developed to describe this physical feature was

$$H = 664 \exp(-0.197n) + 48p \tag{26}$$

where:

n = number of carbon atoms in the original alkyl phosphate
$(8 < n < 16)$
p = concentration of the solution (wt. %)

Maximum foam stability of the homologous alkyl phosphate solutions was greater than 90%. The concentration of mono- and/or didodecyl with alkyl phosphates can be manipulated to give the optimal foam height.

Foam stability is influenced by pH (Lauwers & Ruyssen, 1964). Protein solutions of pure β-lactoglobulin showed marked pH influence. A sharp minimum in foam stability occurred at the pH associated with the isoelectric point of the protein. A positive value for the coefficient of spreading was necessary for foam inhibition. Interestingly enough, foam stability showed a sharp increase where pH = 7 for senegin solutions (Joos & Ruyssen, 1964).

The foam stability criteria number 4, presented previously, was adopted by Joos & Ruyssen (1964) in their experiments using senegin, which is purified saponin extracted from selected roots of the Polygala Senega. Low gas flow rates produced more stable foams characterized by regular-shaped bubbles. Foam stability decreased as the concentration increased. Addition of 10^{-4}N NaCl also increased foam stability but concentrations higher than 10^{-2}N decreased the stability.

Burcik (1950) also found NaCl addition affected foam stability on his solutions of sodium laurate. His value of the turning point as a stabilizer/inhibitor was 0.01N, which is a much higher concentration than Joos & Ruyssen. This difference can be attributed to the different surfactants used by each researcher. Other findings of Burcik included:

1. Sodium laurate. Foam stability occurred in the concentration range of 0.02N to 0.025N. This coincided with surface tension being low and at the optimal rate of surface tension lowering.
2. Sodium dodecyl sulfate. Concentration range of 0.005N to 0.03N showed foam was unstable due to high surface tension.
3. Sodium oleate. Foam stability increased with increased concentrations until a plateau was reached, thereafter, foam stability was independent of concentration.
4. High foam stability favors: (1) low surface tension in relation to

that of the pure solvent, (2) moderate rate of surface tension lowering and (3) high bulk or surface viscosity.

Summary

The effects of surfactants on surface tension and foaming are currently being investigated. The amount of information in these areas is tremendous and needs to be compiled. Topics which need to be correlated include (1) surfactant characteristics and surface tension and (2) surfactant characteristics Table 6 summarizes the dynamic surface tension measurements made on various solutions.

Table 6. Surface Tension Measurements of Surfactant Solutions

Surfactant	Method	Concentrations	Time Interval	Comments	Reference
Sodium dodecyl sulfate	Drop-weight	3.3 5.9 $\times 10^{-3}$ M 25°C 8.1	$0 \leq t \leq 150$ sec.	At higher concentrations, lower surface tension values were exhibited for the same surface age.	Kloubek (1975)
	Maximum bubble pressure	1.7 $\times 10^{-3}$ M 25°C	$t < 0.2$ sec.	Surface tension versus bubble intervals (t) and surface age (T).	Kloubek (1972)
		3.3 25°C 3.3 20°C 1.7 $\times 10^{-3}$ M 25°C 1.7 22°C 1.7 20°C	$t < 1.0$ sec.	Increase in temperature corresponded to higher surface tension values for the same surface ages.	
		0.76 0.88 1.70 $\times 10^{-3}$ M 25°C 3.3 5.9 8.1	$T < 0.3$ sec.	Lower concentrations exhibited higher surface tension values for the same surface age.	
		3.3 20°C 3.3 25°C 5.9 $\times 10^{-3}$ M 25°C 8.1 25°C	$T < 0.015$ sec.		
	Oscillating jet	5.0×10^{-3} M	$t < 0.08$ sec.		Thomas, *et al.* (1975)
		4.0×10^{-3} M		Recrystallized and foam fractionated solutions.	Gilanyi, *et al.* (1976)
		4.1×10^{-3} M		Recrystallized.	
Hexadecyl sulfate	Drop-weight	6.1×10^{-6} M	$t < 600$ sec.	Effects of contaminates on recrystallized SDS solutions.	Gilanyi, *et al.* (1976)
Lauryl alcohol		3.1×10^{-6} M			

Table 6. (Cont.) Surface Tension Measurements of Surfactant Solutions

Surfactant	Method	Concentrations	Time Interval	Comments	Reference
Sodium di-(2-ethylexyl) sulphosuccinate	Oscillating jet	0.05g/100cm^3	$0 \leq t \leq 0.070$ sec.		Thomas, *et al.* (1976)
Heptanoic Acid	Drop weight	1.5x10^{-2} M	$1 \leq t \leq 1000$ sec.	Definite minimum surface tension value exhibited after which surface tension increased.	Pierson, *et al.* (1976)
Hexanoic Acid		8x10^{-2} M	$1 \leq t \leq 1000$ sec.		
Dimethyl-decylphosphine oxide (DC$_{10}$PO)		0.00063% 0.0024% 0.0068% 0.014% 0.048% 0.137%		Various stalagmometers were used. Shows $\frac{\gamma_o-\gamma}{C_o} \times 10^3$ vs. $\sqrt{t}$ γ_o = initial surface tension (not necessarily at t = 0) γ = surface tension at time t C_o = initial surfactant concentration	
Dimethyl-dodecyl phosphine oxide (DC$_{12}$PO)	Maximum bubble pressure	0.00066% 0.0015% 0.0030% 0.0060%	$10 \leq t \leq 100$ sec.	Plots revealed straight lines for each surfactant at all experimental concentrations. A diffusion model was presented.	Bendure (1971)
Dimethyl-dodecylamine oxide (DC$_{12}$AO)		0.001% 0.0021% 0.0039% 0.0064% 0.013% 0.020% 0.056%			
N-dodecylhexaoxyethylene glycol monoether (C$_{12}$E$_6$)		0.00058% 0.00083% 0.0024% 0.0034% 0.0076%			

Table 6. (Cont.) Surface Tension Measurements of Surfactant Solutions

Surfactant	Method	Concentrations	Time Interval	Comments	Reference
Dodecylamine Hydrochloride	Maximum bubble pressure	$5x10^{-3}M$			Kloubek (1972)
Carbowax 6000		0.025 0.075 0.10 0.25 g/cm^3	t < 0.060 sec.	Low concentrations exhibited higher surface tension values for the same surface ages. Higher concentrations had greater changes of surface tension with time. Noticeable was a local maximum surface tension value after an initial decline.	
Carbowax 1540	Oscillating jet	0.005 -0.01 0.025 0.10 g/cm^3	t < 0.060 sec.		
Sodium Di-(2-ethyhexyl) sulphosuccinate		0.075 0.0875 0.10 g/cm^3	t < 0.060 sec.		Thomas, *et al.* (1975)
Teepol L		0.25 0.50 5.0 g/cm^3	t < 0.060 sec.		
Cetyltrimethylammonium bromide		0.025 0.050 0.10 0.18 g/cm^3	t < 0.0.060 sec		

OXYGEN TRANSFER

General Considerations

The proposed effect of surfactants on oxygen transfer is two-fold. First, the adsorption of surfactants onto the gas/liquid interface decreases the available surface area for molecular diffusion. Second, the formation of the hydration layer at the surface, resulting in higher surface viscosity and increased thickness of the surface layer, increases the resistance to oxygen transfer. Both mechanisms support the premise of the decrease in oxygen transfer in the presence of surfactants (Mancy & Okun, 1965).

Surface tension lowering due to surfactants can in some cases increase oxygen transfer due to hydrodynamic changes in bubble characteristics. The decrease in surface tension breaks the larger bubbles formed from submerged aerators, into smaller bubbles as they rise to the surface. The resulting increase in surface area for diffusion allows for more oxygen transfer and support the results of the higher oxygen transfer rates.

Relating K_La to bubble diameter, Barnhart (1969) showed increasing K_La for bubble diameters <0.22 cm, then K_La decreased for bubble diameters > 0.22 cm. The bubble size reduction was limited by the critical micelle concentration of the surfactant on the surface of the bubble. Concentrations higher than the critical micelle concentration may change the diffusivity constant as well as bubble characteristics, thus explaining the drop in oxygen transfer.

The smaller bubble sizes observed in aerated surfactant systems show slower rise velocities than the same bubble size in tap water. This effect can be attributed to decreased internal circulation of gas in the bubble (Motarjemi & Jameson, 1978) and increased liquid drag forces because of higher surface viscosities (Mancy & Barlage, 1968). The decreased velocity of the bubbles, leading to longer retention times in the tank, promotes oxygen transfer. Bubble velocity has been correlated to a modified Reynolds number. Barnhart (1969) summarized the results as follows:

$R < 300$	Spherical bubbles act as rigid spheres. The rise is characterized as rectilinear or helical.
$300 < R < 4000$	Bubbles have ellipsoidal shape. The rise is characterized as rectilinear, rocking motion.
$R > 4000$	Bubbles formed spherical caps.

Detwiler (1979) found adsorption of surfactants on air bubbles directly affected the rising speed of the bubbles. A surface tension gradient developed on the surface of the rising bubble such that higher surface tension values were located on the top of the bubble. This gradient resulted from surface renewal and promoted the formation of a rigid cap. The terminal rise velocity corresponded to an equilibrium cap size. For a given surfactant, the completely rigid sphere can be associated with a given bubble size. The time to reach terminal velocity increased with bubble size and with low surfactant concentration.

Mancy & Barlage (1968) proposed two categories for the effect of surfactants: surfactant film surrounding the air bubble, and change in hydrodynamics (shape and bubble dynamics) at the interface. They used the oscillating jet to determine surface tension of surfactant solutions, using the Gibbs isotherm, were able to calculate the instantaneous concentration of surfactants at the interface. Knowledge of the instantaneous total mass transfer resistance enabled them to calculate instantaneous liquid film resistance below the surface. The rate of adsorption affected oxygen transfer.

Characteristics of surfactants on oxygen transfer have been investigated by Lynch & Sawyer (1960). A summary of their findings include:

1. The higher number of carbon atoms (n) in the alkyl group of surfactants polypropylene benzene sulfonate, straight-chain alkyl benzene sulfonates with attachment at the second carbon atom and normal straight-chain alkyl benzene sulfonates, decreased the gross oxygen transfer coefficient for the same concentration of surfactants in different synthetic waters. The normal straight-chain alkyl benzene sulfonates showed an increase in the volumetric oxygen transfer coefficient starting from n = 10 - 12 in synthetic waters of known hardness. This reversal in trend was attributed to insolubility of the surfactant in the solution.
2. The length of the hydrophilic ethylene-oxide group in nonionic fatty esters affected oxygen transfer. The large ethyoxy group corresponded to lower oxygen transfer coefficient. For nonionic fatty amides, longer ethyoxy group corresponded to higher value of K_La.
3. Ionic nature and chemical configuration of the hydrophilic group was important.

Implications for Oxygen Transfer

One of the most important topics in wastewater treatment systems using aeration basins is the efficiency of oxygen transfer. Low oxygen transfer translates to high energy costs, often substantial, since aeration power costs generally comprise the majority of treatment costs. The effect of surfactants on oxygen transfer in pure solvents with surfactants has not be definitive: increased, decreased and no change situations have been noted (Hwang & Stenstrom, 1979).

Oxygen transfer can be expressed as

$$\frac{dm}{dt} = K_L a(\overrightarrow{C}^{*}_{\infty} - C) \tag{27}$$

where:

dm/dt = oxygen transfer

K_L = diffusivity constant for the gas in the liquid

A = surface area through which diffusion occurs

C = concentration of the gas in the liquid

$\overrightarrow{C}^{*}_{\infty}$ = equilibrium concentration of the gas in the liquid

This equation is not used in wastewater oxygen transfer because the area is difficult to quantify since it is comprised of the summation of the surface area of all bubbles in the tank as well as the surface area of the basin at the liquid/gas interface. Furthermore, atmospheric pressure and hydrostatic pressure control the expanding surface of the rising bubble and the saturation concentration. The equation

$$\frac{dC}{dt} = K_L \frac{A}{V} (\overrightarrow{C}^{*}_{\infty} - C) \tag{28}$$

is derived from the substitution

$$\frac{dm}{dt} = (\frac{dC}{dt})V \tag{29}$$

V = volume

The same problems of the previous case still exist with the use of this equation. A lumped parameter, $K_L a$, eliminates this problem:

$$\frac{dC}{dt} = K_La(\overline{C}_\infty^* - C) \tag{30}$$

where:

K_La = volumetric coefficient of oxygen transfer or overall mass transfer coefficient (t^{-1})

Present oxygen transfer research has been to determine K_La. In wastewater treatment systems, K_La has been correlated to α where $\alpha = \frac{K_La_{ww}}{K_La_{tw}}$, with ww denoting wastewater and tw denoting tap water. K_La is usually calculated from the unsteady-state clean and dirty water reaeration test. Since α depends on wastewater characteristics and heavily on the method of aeration, nothing more than a general qualitative correlation has been developed. Typical values of α for surface aerators is 0.8 to 1.0, whereas the value ranges from 0.3 to 0.6 for fine bubble porous diffusers.

The implication of using dynamic surface tension in oxygen transfer systems is the possible emergence of a new parameter to correlate K_La_{ww}. It appears the functional relationship of K_La and surface tension versus time of bubble formation are similar, i.e., both decrease exponentially with time and it may be possible to correlate K_La to dynamic surface tension measurements. The benefit derived from this correlation is the elimination of the dirty water unsteady state test.

If a correlation between dynamic surface tension and K_La exists, then K_La_{tw+s} and K_La_{ww} (tw+s = tap water + surfactants) can be determined in the laboratory or factory shop test facility by one of the dynamic surface tension measuring techniques previously mentioned. K_La by this method is solely a function of water quality rather than aeration method or basin configuration. It would, therefore, also be necessary to determine $(K_La_{tw+s})_b$ (K_La of the aeration basin) using the unsteady-state test to account for the actual physical configuration and aeration method. The new correlated parameter looks like

$$\alpha_{\text{full-scale system}} = \frac{K_La_{ww} \text{ as a function of dynamic surface tension}}{K_La_{tw+s} \text{ as a function of dynamic surface tension}} \quad (31)$$

The British have used surfactant concentrations of 5 mg/l in clean water testing for K_La and it is suggested that procedure should be continued for this proposed method. Furthermore, the concentration of surfactant used in $(K_La_{tw+s})_b$ and K_La_{tw+s} be the same. Note that the dynamic surface tension of the surfactant solution obviously is the same for a given type and concentration of surfactant at a given temperature; therefore one set of values for this test is sufficient for the determination of $(K_La_{tw+s})_b$.

Although this proposal allows for rapid calculation of $(K_La_{tw+s})_b$ and has the advantage of not disrupting basin operations as in the unsteady-state test, there are marked disadvantages. The most serious is the calculation of K_La for both wastewater and surfactant solutions for the time of bubble formation. Careful experimental design is required to avoid appreciable experimental error in measuring solution oxygen concentration for all bubble formation times. Another disadvantage is the instantaneous aspect of the dynamic surface tension measurement and its extrapolation to basin $(K_La_{tw+s})_b$ since the latter is a function of aeration time and location in the basin.

CONCLUSIONS AND RECOMMENDATIONS

Static and dynamic surface tension measurement were discussed. It is evident that static surface tension measurements cannot be used for surfactant solutions because of the time-dependence of surface tension until equilibrium is established. It is not, however, possible to use the results obtained by any dynamic measurement unless a correction factor is used to scale the values into the acceptable range. The "correction factor" for the oscillating jet is the careful selection of orifice based upon surface tension values obtained from a pure solution. Reliance of the accurate dead time is the maximum bubble pressure "correction factor" and drop methods rely on the Harkins and Brown correction factor. Correction factor dependence indicates the methods may not produce absolute values of surface tension. Static and dynamic surface tension measurements were discussed.

What has become apparent during this study is the quantity of literature available on surfactants. The bulk of the material seems to deal with surfactant properties rather than the effect of the surfactant on various uses; little has been done to determine their effects on oxygen transfer. This also leads to the observation that with the rise in the number and quantity of surfactants in use today, its effect on the wastewater treatment process may be more pronounced in the future.

The proposal of Mancy & Barlage (1968) to determine the effects of surfactants on oxygen transfer using dynamic surface tension measurements should be studied further. The oscillating jet method results in the surface tension calculation at very early ages of the surface, so the effect of diffusion of the surfactants to the surface can be observed. The Gibbs isotherm relates surfactant surface concentration to surface tension, therefore the effect of the surfactants on the bubbles can be observed. This is the first effect they discuss of surfactants on solutions.

It is suggested that the maximum bubble pressure method be used as the technique to measure dynamic surface tension. This method, more than any other dynamic surface tension technique, closely models the actual physical state occurring in aeration basins, although only individual bubbles are recorded. It is also the only method viable as a portable field unit; it can be compact and doesn't require the sophisticated equipment needed for the oscillating jet method. The drop methods may be viable as a portable field unit except the technique is subject to more inaccuracies than the oscillating jet or the maximum bubble pressure methods and evaporation of the drop surface must be prevented. Another advantage of the maximum bubble pressure method, over the oscillating jet method, is its ability to measure longer surface ages. Furthermore, the cost of this method would appear to be much less than the oscillating jet.

Other general recommendations:

1. The number of articles dealing with surfactants or surfactant-related topics appears to be endless. Much more research can be done in this area, especially by way of summaries or literature reviews on specific surfactants or surfactant properties. There seems to be no comprehensive current state-of-the-art general review on surfactants except by Rosen (1978), which is excellent. Rosen, however, does not address the study of surfactants from the oxygen transfer view, thus, it serves only as a good starting point for future research.

2. Work started by Lynch & Sawyer (1954, 1960) on the effect of surfactants on foaming and on oxygen transfer should be continued. Specifically, a list of surfactant characteristics and its effect on oxygen transfer should be developed.

3. As seen from the above, since foams are closely related to surface tension, a possible correlation between dynamic surface tension and foaming, or foam stability, should be investigated. In addition, a standard method to measure foam stability should be initialized.

A goal of current research is to develop a relationship between oxygen transfer and dynamic surface tension measurements. It is believed that at very early surface ages oxygen transfer might be correlated with the expanding bubble surface. Oxygen transfer rates are the highest at the expanding bubble surface, then decline to a steady-state value at constant bubble size (Okun & Baars, 1964).

The previous section has shown that perhaps a new type of correlation factor can be devised from the relationship between oxygen transfer and dynamic surface tension. The variables requiring the most attention are K_La_{tw+s} and K_La_{ww}. Initially these must be experimentally determined, therefore careful experimental design is necessary to insure reliable results. It is hoped that a correlation will emerge between K_La_{tw+s} and dynamic surface tension such that the surface tension measurements alone would accurately predict K_La_{ww}. If this is possible then perhaps the $(K_La_{ww})_b$ can be determined without the unsteady-state reaeration test. Research in this area has commenced and needs to proceed to a definite conclusion via experimentation.

Dynamic surface tension values have been used as a measure of surfactant concentrations at the interface. This led to models of surfactant transport and the calculation of the liquid-side coefficient of mass transfer resistance. More research in this area would lead to more understanding of interfacial mass transport phenomena. Careful selection of experimental technique will, at the same time, yield information about surfactant characteristics and mass transfer.

The relationship between oxygen transfer (aeration basin and theoretical), dynamic surface tension and surfactants are complex and have just begun to be recognized. Future goals in this area should include the deciphering of more relationships so oxygen transfer in basins could be better anticipated. The additional knowledge gained by these interrelationships can only improve the economical efficiency of the aeration process.

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