Dynamic Surface Tension Effects on Oxygen Transfer

By Gail K. Masutani[1] and Michael K. Stenstrom[2]

Abstract: Recent advances in estimating mass transfer coefficients are largely restricted to clean water conditions, and engineers must still rely upon empirical methods such as α factors to correct results for process conditions. This research focuses on quantifying the volumetric mass transfer coefficient, K_La, and the liquid film coefficient, K_L, using the dynamic surface tension (DST) measurement. Two anionic surfactants are used in two concentrations to observe their effects on diffused air and to characterize the DST relationship. A mathematical model is formulated showing the DST relationship with bubble life, as a function of two parameters, slope and intercept of the DST function. DST value is calculated from the model using the estimated parameters and the bubble retention time. K_La is predicted by DST, aeration flow rate, and the static surface tension measurement. The final result shows the DST parameter can estimate K_L values given the air flow rate and surfactant concentration.

Introduction

An important goal of environmental engineering research is to increase oxygen transfer efficiencies. Strategies include modifying aeration basin geometry, diffuser placement and type, water depth, or aerator selection, and changing process operating conditions. Manufacturers optimize their equipment using clean-water, shop oxygen-transfer tests; however these tests often fail to adequately predict operation under process conditions. Errors usually result in substantial additional aeration costs to meet oxygen demand.

Alpha (α) (the ratio of the overall volumetric mass transfer coefficient of process water to tap water), is the parameter of interest in this study. Although α is dependent on basin geometry, liquid properties, and aeration type, it is used to extrapolate lab results in scale-up operations and to predict oxygen transfer in process water. With α's dependence on such varied conditions, it is no wonder that its predictive performance falls short of the actual operational needs.

The main reason for the unpredictability of α is that it is defined through mass transfer theories that are imperfect. The mass transfer coefficients used to obtain alpha factors are based on the Lewis and Whitman's (1924) two-film theory. For sparingly soluble gases, the liquid film controls diffusion and the concentration of the gas at the liquid film interface is in an equilibrium with the gas phase as defined by Henry's law. The concentration of the gas in the bulk liquid is assumed to be uniform. Alpha is constructed on this steady-state theory, which is inherently imperfect since the concentration at the interface is not constant. Higbie's (1935) penetration theory and Dankwerts' (1951) surface renewal theory more closely approximate the

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actual transfer mechanisms, but are generally not used in aeration practice. The steady-state two-film theory is used because of its utility for parameter estimation.

The mass transfer coefficients need to better reflect actual field conditions. Alpha factors have limited utility because they neglect the effect of varying rates of surfactant adsorption to the bubble/water interface, since they are based upon steady-state theory. More advanced approaches require knowledge of the time-dependent nature of mass transfer and the rate of surfactant adsorption.

Static surface tension measurements have been used to predict to α values with inconclusive results (Stenstrom and Gilbert 1981). Dynamic surface tension (DST) incorporates the time-dependent nature of surfactant adsorption and holds promise for improved oxygen transfer prediction, but the relationship between DST and oxygen transfer efficiency has not been investigated.

The goal of this research is to correlate the mass transfer coefficient with a parameter that characterizes the liquid parameters. It is believed such a parameter can be identified by DST. When this transfer parameter is identified, it will better correlate the mass transfer coefficient such that engineers can better predict aeration system performance.

Surface Tension Measurements

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 ease of calibration (Freud and Freud 1930). Surface tension is measured by the mechanical force necessary to lift a platinum ring of known wire radius and ring radius from the solution surface. Huh and Mason (1975) presented a rigorous theory of ring tensiometry and concluded that the ring method produced excellent results for surface tension measurement when using the Harkins-Jordan correction factors.

Although there are many dynamic surface tension measuring techniques, the maximum bubble pressure method was selected for this investigation because of its measuring range and low costs (Masutani 1988). The maximum bubble pressure method (Sugden 1922) is based on the maximum pressure in a capillary or a maximum pressure difference between two capillaries of different radii when producing and detaching a bubble from a capillary tip immersed in a test solution.

Surfactants and Oxygen Transfer

Surfactants adsorb at the gas/liquid interface in a constructed, usually charged, monolayer. At the critical micelle concentration (CMC), the adsorbed film is most compact (highest surfactant concentration per unit of interfacial area) and the monolayer has the maximum thickness. If surfactant concentration is increased beyond the CMC, a multilayer of molecules adsorbs at the interface (Mancy and Okun 1960). Surfactants tend to: (1) Stabilize the interface, making the gas/liquid interface more rigid (Lister and Boon 1973); (2) decrease surface renewal (Eckenfelder et al. 1956); and (3)

increase interfacial viscosity (Mancy and Okun 1960; Yoshida and Akita 1965).

Mancy and Okun (1960) noted as surface active agents (SAA) concentration increased, the time of bubble formation and bubble volume decreased. Both can be explained by lower surface tension values in the presence of SAA, which decrease the elasticity of the interface so shear forces make smaller bubbles at a faster rate. The smaller bubbles also have greater retention times and more total surface area. The adsorption of the surfactants onto the gas/liquid interface decreases the film coefficient K_L. Surfactants at the interface decrease the available surface area for molecular diffusion, and form a hydration layer at the surface, resulting in higher surface viscosity and increased thickness of the surface layer, which increases resistance to oxygen transfer. Both mechanisms support the premise of the decrease in oxygen transfer in the presence of surfactants (Mancy and Okun 1965). The mechanisms are complex as indicated by conflicting evidence reported by Carver (1956), who observed a decrease in K_L in surfactant solutions even though the reduction in shear forces at the boundary layer resulted in decreased terminal rise velocity, reduced oscillatory motion, and increased drag.

Mancy and Barlage (1968) extended Mancy and Okun's (1960, 1965) work and concluded surfactants are effective at reducing gas transfer rates and that the reduction is dependent on the aeration technique. Furthermore, mass transfer reduction, whether due to a physical barrier inhibiting diffusion through the interface or to formation of the hydration layer, is largely a function of the structure and physiochemical characteristics of the surfactant molecule as well as aeration technique.

Two opposing mechanisms affect the overall transfer of oxygen in aeration. The increase in surface area promotes transfer, whereas the decrease in K_L inhibits transfer. Mancy and Okun (1960) indicated higher K_La values are obtained in the presence of surfactants. They showed K_L decreased sharply with increasing surfactant concentration until the CMC, after which K_L remained unchanged with further surfactant concentration increases. However, K_La continued to increase with increasing surfactant concentration, indicating the total surface area overcompensates for the reduction in K_L. Others contend the increase in surface area does not offset the decrease in K_L (Lister and Boon 1973; Otoski et al. 1978; Eckenfelder et al. 1956).

Eckenfelder and Ford (1968) also show the degree of mixing plays a role in determining oxygen transfer. Under laminar conditions when the stagnant film theory dominates, the α value is unaffected because the interfacial resistance to transfer is less than the resistance in the bulk solution. As turbulence increases, α decreases because the interfacial resistance governs the transfer rate. At highly turbulent conditions, α increases since the surfactants cannot establish an interfacial film for mass transfer resistance, allowing high surface renewal rate.

A consequence of surface tension reduction with surfactants, especially in aerated wastewater treatment systems, is the production of foam. Little research has been conducted on foaming effects or the effects of an antifoam agent on oxygen transfer. Lynch and Sawyer (1954) found no correlation between the type of surfactant (anionic or ionic) and foam production (or nonproduction). They noted frothing is temperature dependent with warmer temperatures promoting more foam production.

Experimental Procedures

Dynamic Surface Tension Apparatus

The experimental equipment was patterned after Bendure's (1971) device shown in Fig. 1. The bubble formation process starts with water flow from the constant head reservoir through a rotameter, and into a water trap chamber that forces air out as the new working fluid. After passing through a desiccator, the air is released through a submerged glass capillary tip forming bubbles in an aqueous solution. An inclined manometer allows visual observation of system pressure. The differential pressure transducer's signals are sampled and recorded using a personal computer. Another pressure transducer (not shown) monitors relative changes in barometric pressure during an experimental run.

Bubble formation and release can be described as a series of spikes on the strip chart recorder. The voltage output is converted to pressure readings through daily transducer calibration tests. The maximum bubble pressure is the recorded bubble pressure minus a friction factor, which compensates for flow resistance in the apparatus. Fig. 2 is typical representation of the data collected for one point on the dynamic surface tension measurement (DST) curve. Bubble formation time (bubble life) is taken as the averaged time interval between successive peaks. The corresponding surface tension is the averaged value of those peaks for that flow rate.

Sugden (1922, 1924) developed the maximum bubble pressure measurement for surface tension. He showed that the maximum pressure (P_{max}) to form a bubble is a function of the capillary radius (r), hydrostatic capillary depth (P_t), surface tension of the solution (γ), radius of curvature of the bubble (b), the maximum depth of the bubble (z_{max}), and the difference between fluid and gas density ($\Delta\rho$).

$$P_{max} = \frac{2\gamma}{b} + \Delta\rho g z_{max} + P_t \quad (1)$$

Aeration Apparatus

The aeration studies were performed in a 208 L tank with baffles using two fine bubble diffuser stones as shown in Fig. 3. Two dissolved oxygen

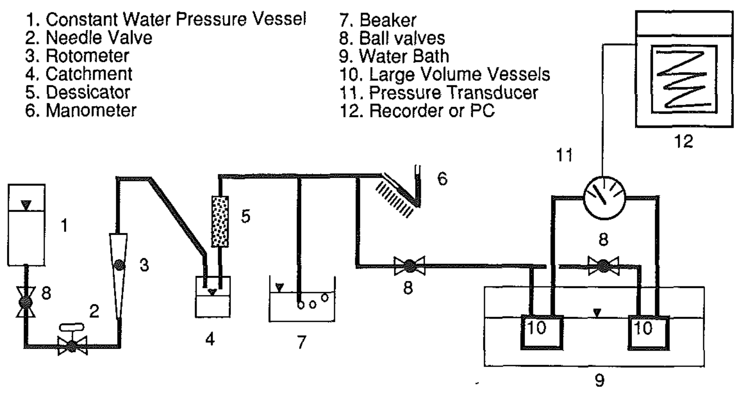

FIG. 1. Dynamic Surface Tension Measuring Device

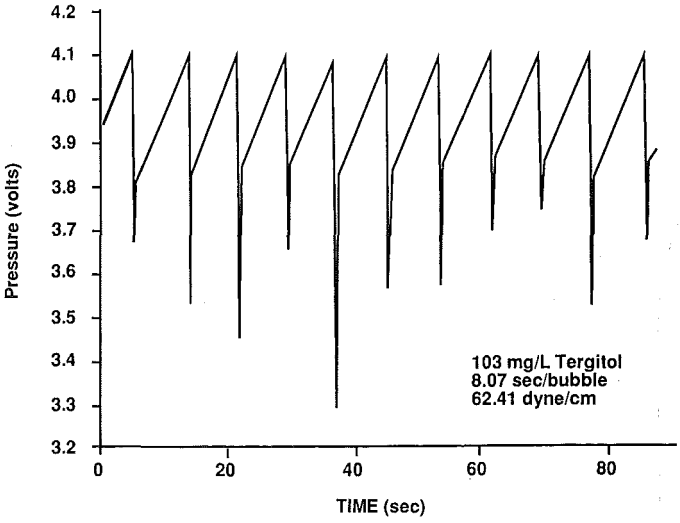

FIG. 2. Typical Bubble Patterns

meters and probes were used to measure the dissolved oxygen in the tank. The probes were calibrated before each use by the Winkler-Azide modification method. The water was deoxygenated by a combination of nitrogen stripping and cobalt-chloride sodium-sulfite reaction to keep the dissolved solids concentration low. Water was replaced in the tank before the dissolved

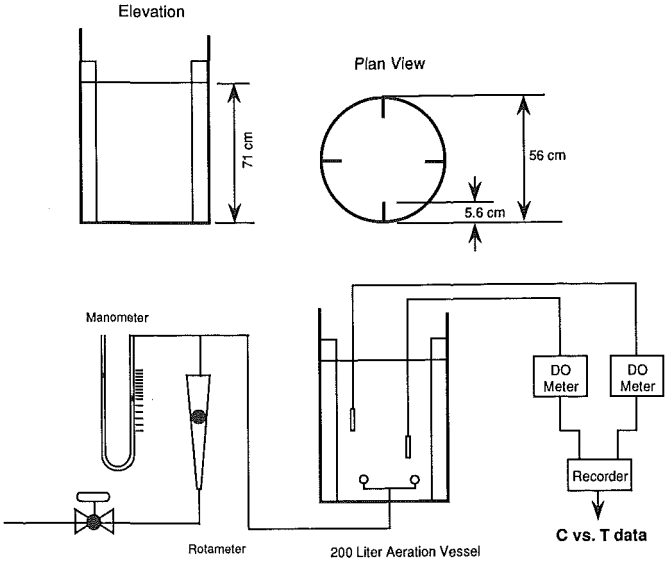

FIG. 3. Aeration Equipment

solids concentration reached 1,500 mg/L. All other procedures conformed to the ASCE Standard ("A standard" 1984).

The dissolved oxygen meters were connected to a linear strip chart recorder for monitoring and permanent recording. K_La, saturation concentration, C^*_∞, and initial concentration, C_I were estimated for each probe and an overall K_La was obtained by averaging each probe's K_La. Dodecyl sodium sulfate (DSS) and tetradecyl sodium sulfate (under the Union Carbide trade name of Tergitol 4) were the surfactants chosen for this study.

Bubble Diameter Measurement

A clear acrylic 0.3 m × 0.3 m × 0.9 m box was used as an aeration vessel to determine bubble sizes. Bubbles formed in clean water and surfactant solutions were photographed using a 35-mm SLR camera fitted with a 50-mm macro lens. A ruler with 0.01-in. gradation was also photographed to provide a measuring reference. Bubbles were successfully photographed at each flow rate at a shutter speed of 125 s^{-1} with an automatic electronic flash.

DST Measurement

The first experiments using the DST measuring device were performed on tap and bottled water. Pure water has a surface tension value of 72.75 dyne/cm at 20° C (Harkins 1952). Deviation from this measured value using the DST device is attributable to experimental errors such as the effects of head losses (friction) and are collectively termed friction factor (ff). The deviation in the measured surface tension from the known surface of pure water was estimated from measurements over representative bubble times, as follows:

$$\mathrm{ff} = \sum_{j=1}^{n} (72.75 - \gamma_i)_j \qquad (2)$$

where: γ_i = surface tension value obtained by DST device at flow rate i; n = total number of runs; and j = run number.

The friction factor was calculated on bottled drinking water. Eq. 2 uses the pure water surface tension values as a reference. Although bottled drinking water is not pure water, this substitution was an affordable compromise that yielded more consistent results than with tap water. If experimental conditions remained fixed, the friction factor should be constant, but this was usually not observed. From the magnitude of the observed bubble pressures, the daily changes in barometric pressure may interfere with the pressure transducer readings and thus, could cause the observed fluctuations in the friction factor. This needs further investigation.

The friction factor was in the range of ±3 dyne/cm, which is about 4% of the static surface tension value of water. This correction factor was applied to all observed DST measurements taken on the same day in an attempt to minimize the day-to-day variations obtained under otherwise identical conditions.

Dynamic Surface Tension Function and Model

The dynamic response of a surfactant on surface tension is shown in Fig. 4. Surfactants decrease surface tension values with increasing bubble age

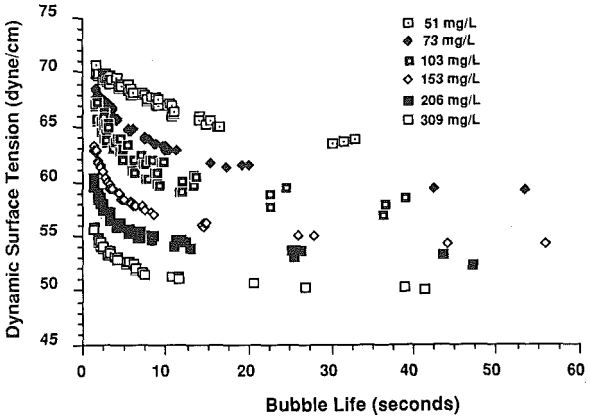

FIG. 4. Dynamic Surface Tension as Function of Tergitol Concentration

because more time is allowed for surfactant adsorption. Similarly, lower surface tension values for the same bubble life at higher surfactant concentrations results from greater surfactants adsorption, as indicated by steeper DST curves.

An equation to describe the data was developed by an observation in the formulation of Bendure (1971). He presented two diffusion-controlled adsorption equations relating dynamic surface tension measurements to bulk surfactant concentrations and to bubble life. For long adsorption times, >2.8 s, which obey Langmuir isotherms:

$$\gamma - \gamma_\infty = \frac{\Gamma_m^2 RT}{\sqrt{\pi D} C_0 \sqrt{t}} \quad \ldots\ldots (3)$$

where γ_∞ = equilibrium surface tension; D = molecular diffusivity; C_0 = bulk phase concentration; Γ_m = saturation surfactant concentration; R = gas constant; T = temperature; and t = adsorption time. The model can be simplified by combining terms as follows:

$$\gamma - \gamma_\infty = \frac{X}{C_0 \sqrt{t}} \quad \ldots\ldots (4)$$

where X = the lumped parameter (slope) encompassing the surface excess concentration and the diffusion coefficient. By calculating the variable $1/C_0\sqrt{t}$ for all experimental conditions, linear least squares can be used to estimate the infinite-time surface tension value (γ_∞) as the intercept and the X parameter as the slope. Forty-five data sets on Tergitol showed slightly better correlation ($>r^2$) at higher surfactant concentrations, indicating better model fit with greater slope at lower bubble life. All the correlation coefficients were greater than 0.82.

An analysis of X versus the du Nouy surface tension is shown in Fig. 5. The value of r^2 was greater than 0.87 for both DSS and Tergitol. Fig. 5 indicates higher surfactant concentrations correspond to greater X parameter

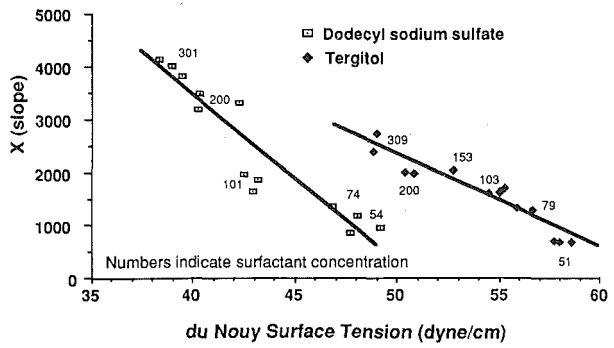

FIG. 5. X versus du Nouy Surface Tension for Unaerated Solutions of Tergitol and Dodecyl Sodium Sulfate

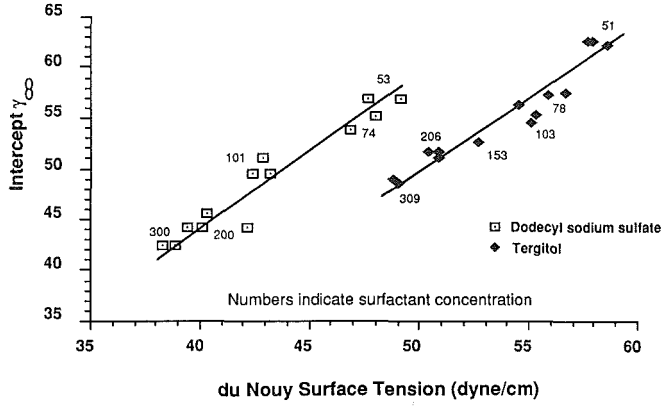

FIG. 6. Intercept versus du Nouy Surface Tension for Unaerated Solutions of Tergitol and Dodecyl Sodium Sulfate

values, as expected from adsorption theory. It is more probable at high surfactant concentrations that more surfactant molecules will adsorb at the interface than at low surfactant concentrations for the same period of time. More surfactants at the surface indicates lower surface tension values, steeper DST curves, and higher X values.

Another indicator of the model fit is the correlation between DST prediction at infinite time (γ_∞) and the du Nouy measurement, which is shown in Fig. 6. The intercept of the model is the infinite time surface tension value (γ_∞), which should be the equilibrium surface tension value, i.e., the du Nouy measurement. The values of r^2 for both Tergitol and DSS were greater than 0.92.

These correlations are useful in simplifying the model shown in Eq. 4, which requires the initial surfactant concentration, C_0. It is not practical to always measure initial surfactant concentration, C_0. By substituting $X' = X/C_0$ the model simplifies to:

$$\gamma - \gamma_\infty = \frac{X'}{\sqrt{t}} \quad (5)$$

PRELIMINARY AERATION RESULTS

Surfactant Concentration Gradients

The observation of changing mixing patterns (Hwang and Stenstrom 1979) in the aeration basin with changing surfactant concentrations has led to speculation of the existence of surfactant gradients in the mixing patterns. Until recently, there has been no method to verify this observation; however, DST is able to detect surfactant concentration gradients in the aeration vessel. Visual evaluation of the DST curve or calculated X values reflect the apparent differences in surfactant concentrations between samples taken from the top and bottom of the tank. As shown previously, the higher X values, corresponding to a steeper DST curves, indicate higher surfactant concentrations.

Table 1 summarizes the results of DST calculations on the top and bottom samples of 200 mg/L Tergitol solutions aerated under various flow rates. A cut-off level of 4% (significance = 0.04) difference from the mean of the top and bottom measurement was the criterion used to determine placement in the categories.

The majority of the samples fall into the "no change" category, indicating the apparent lack of surfactant gradients. This complete mix condition may be the result of the shallow water depth of the test vessel and high air-flow rates. The lack of conclusive surfactant gradient patterns in the aeration tank may also be attributed to changing mixing patterns in the tank. Hwang and Stenstrom (1979) noted two different water circulation patterns for identical surface aeration designs at the same surfactant concentrations and cited examples where two different mixing patterns had resulted in failures at full-scale plants. For certain correlations the top-to-bottom patterns would shift to top-half and bottom-half cell circulation patterns with no interactive mixing for minimum changes in mixing energies. This observed phenomena may explain why surfactant gradients exist between the top and bottom of the tank, but no pattern was established for the direction of the concentration gradient as a function of flow rate. What has been established is the use of DST to detect apparent surfactant concentration differences.

Although these conclusions are applicable only to this aeration design, some form of surfactant concentration gradient is expected for most basin geometries and aeration techniques. Careful investigation of possible sam-

TABLE 1. Surface Tension Gradients

Aerator flow rate (L/min) (1)	Number of Experiments Showing			
	$X_{bottom} > X_{top}$ (2)	$X_{bottom} < X_{top}$ (3)	No difference (4)	Total (5)
6,050	1	2	4	7
8,050	3	2	8	13
12,000	3	2	2	7
20,000	2	2	3	7

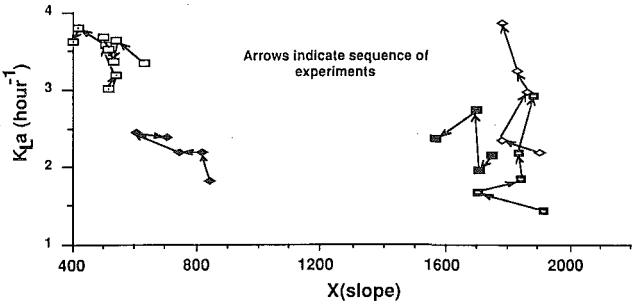

FIG. 7. Effect of Repeated Aeration Experiments on K_La

pling sites is needed to obtain representative X values and must be obtained from the same circulation patterns. A middepth sampling site was selected for this aeration design.

Foaming and Repeated Aeration Experiments

To show the effect of surfactant aging a series of consecutive tests was conducted in the test tank without changing the water or adding fresh surfactant. Fig. 7 shows increasing K_La and slightly decreasing X with repeated testing. This phenomenon can be explained by surfactant deterioration or a gradient in surfactant concentration caused by foaming (Burgess and Wood 1959; Ewing et al. 1979). As repeated experiments were performed, the foam head changed in character and quantity. An early foam appeared as light and airy (large entrapped air bubbles), while after repeated runs, the foam became dense and compact (very small entrapped air bubbles). The changing foam characteristics may indicate surfactant deterioration, which indicates an effective concentration of SAA that is less than the original concentration. This may account for the increasing K_La. The foam character changes may also indicate more surfactants are being drawn from the test solution into the foam. Support for these theories is based on the observation that as the number of experiments with the same test solutions increased, there was a general trend in corresponding decreases in X. The decrease in X translates to a decrease in surfactant concentrations in the test solution.

Foaming of DSS solutions increased the difficulty in accurately determining K_La at a particular solution concentration. K_La increased with almost every test, and after four or five repeated experiments, the increase was significant. Increasing K_La suggests careful experimental procedures must be observed when performing repetitive experiments. The initial surfactant concentration in the aeration basin may no longer be the actual surfactant concentration after four or five experiments. The corresponding measured K_La for each experiment should be correlated with the actual surfactant concentration, not the initial concentration. It appears solutions with high initial surfactant concentrations (100 mg/L) produce greater K_La increases than at the lower surfactant concentration (50 mg/L). This is explained by the greater foam production of the higher surfactant concentration.

British aeration tests, which often use surfactants, have also encountered foaming problems (Burgess and Wood 1959; Downing et al. 1960) even though a concentration of only 5 mg/L was used. This suggests the aeration

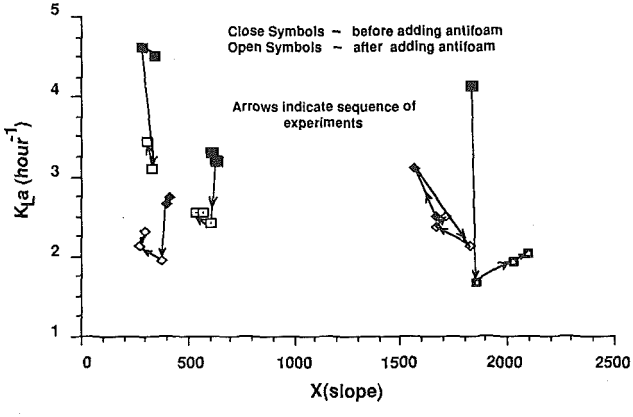

FIG. 8. Effect of Antifoaming Agent on X and K_La

water be changed after every test, which for full-scale testing is impractical. It may be better to select surfactants which produce less foam, such as Tergitol.

Antifoam

An antifoaming agent was used to assess its effect on X and K_La (Fig. 8). Two or three aeration tests on a surfactant solution normally produced a dense and compact foam with corresponding increases in K_La and decreases in X. Addition of 1 ml of an antifoaming agent was sufficient to dissipate the foam, leaving the aeration surface completely foam-free. An immediate reduction in K_La was observed after the addition of the antifoaming agent, and X remained the same before and after the addition of the antifoam agent, except in one case. Using lower surfactant concentration ($X < 1{,}000$), a slight decrease in X was observed, and a slight increase in X was noted using higher surfactant concentration ($X > 1{,}000$). This contradictory trend suggests two different adsorption mechanisms. The decreasing X values imply fewer surfactants are available for surface adsorption, indicating surfactant deterioration. At the higher concentration, there is enough surfactant to overcome the loss due to deterioration and X increases because the dissipated foam head releases surfactants back into the test solution. Further experimentation is necessary to confirm these preliminary results.

The significant reduction in K_La after the addition of antifoam agents suggests care when using these agents. The agent cannot be applied indiscriminately (in volume or location) without first assessing its effects on K_La.

Aeration Results

An important goal of this research is to use DST and other measurable parameters to estimate K_L and/or K_La. To provide a basis for this correlation, experiments were performed at three gas flow rates (8, 12, and 20 L/min) and two surfactant concentrations (50 and 100 mg/L) with both DSS and Tergitol. In view of the results of the previous sections regarding repeated

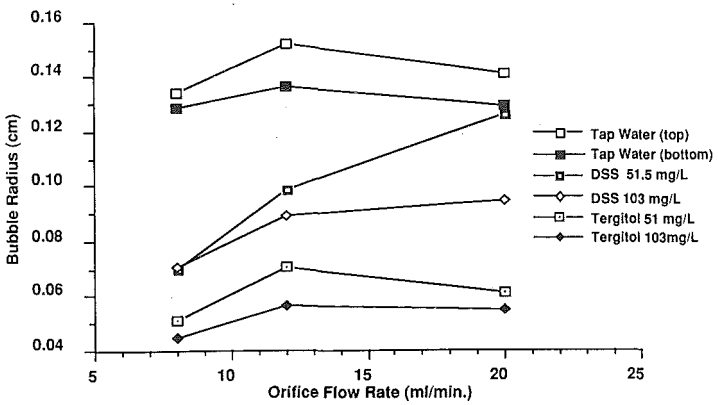

FIG. 9. Bubble Radius versus Orifice Flow Rate

experiments and foaming problems, the experiments were limited to, at most, three repetitive tests. K_La's were corrected to 20° C using a θ factor = 1.024.

Bubble Sizes

Bubble sizes were determined for the surfactant solutions and tap water so the mass transfer liquid film coefficient, K_L, could be calculated from the aeration data. Averaged bubble diameters as a function of flow rate are depicted in Fig. 9. The DSS solutions have larger bubbles than Tergitol solutions and, in general for both surfactants, the higher concentration solutions have smaller bubbles at each flow rate. The large bubble size at 20 L/min for 51.5 mg/L DSS cannot be explained except by bubble coalescence at the high exit velocity at the diffuser stone. This phenomenon was not observed with the Tergitol solution.

K_La and DST Parameters

A series of experiments was performed to determine a relationship between K_La and X. This implies that a relationship exists between surfactant concentration, as indicated by X, and K_La, regardless of the completeness of surfactant adsorption at the air/liquid interface. A relationship between the DST at the mean bubble life is developed later. This relationship accounts for the completeness of surfactant adsorption. Results are shown in Fig. 10 for Tergitol solutions and Fig. 11 for DSS solutions. They show, as expected, as air flow rates increased, K_La increased for the same surfactant concentration. A more defined K_La range is observed at each flow rate for Tergitol solutions than for DSS solutions. This may result from less foaming of the Tergitol solutions, allowing more consistent data to be collected for each experiment.

For surfactant solutions there exists a clearly defined range of DST for each concentration. For both surfactants at 50 mg/L, $600 \leq X \leq 1{,}000$; at 100 mg/L. Tergitol solutions showed $1{,}550 \leq X \leq 2{,}100$, and for DSS solutions, $1{,}900 \leq X \leq 2{,}000$. This again confirms the correlation of high X values with high surfactant concentrations. This result is not the same as in the previous section discussing the model fit. Those surfactant solutions

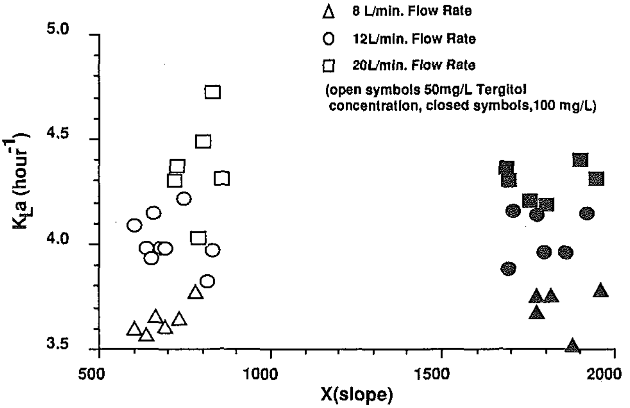

FIG. 10. K_La **versus** X **for Tergitol Solutions**

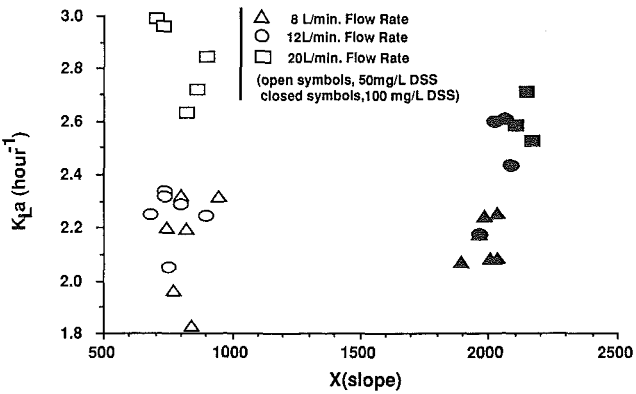

FIG. 11. K_La **versus** X **for DSS Solutions**

were not aerated and this difference probably contributes to the large X range for each concentration in the aerated solution. Aeration causes more interface turbulence and surfactant concentrations as shown earlier may not be consistent throughout the tank. Grab samples tend to have a wider range of X for each concentration and flow rate. This phenomenon, however, needs to be investigated more fully by increasing the number of concentrations and perhaps more careful attention to aeration techniques.

From this discussion, the X parameter alone does not provide adequate correlation to K_La. Therefore an attempt was made to estimate the DST associated with each condition, as a function of surfactant concentration and type, gas flow rate, bubble retention time, and du Nouy surface tension. The DST measurement was calculated as follows:

$$\mathrm{DST} = \gamma_\infty + \frac{X}{C_0\sqrt{t_r}} \quad (6)$$

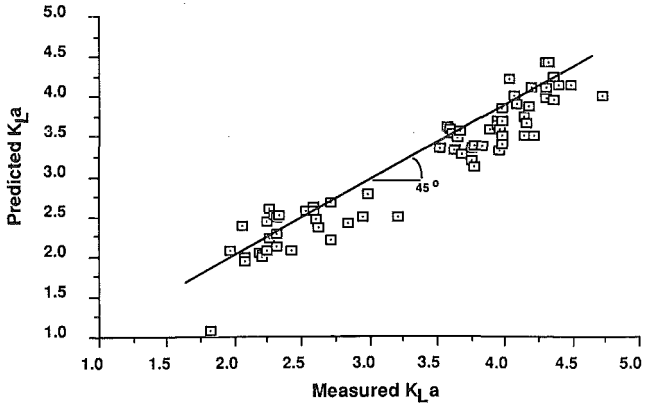

FIG. 12. Predicted K_La versus Measured K_La

where: t_r = bubble retention time in aeration tank; γ_∞ = intercept of linear model (Eq. 4); and X = slope of linear model (Eq. 4) for each aeration sample. The bubble retention time was estimated from the measured rise velocity and the tank dimensions. Fig. 12 shows the correlation, described in Eq. 7

$$K_La = 0.01732 + 0.0009144(\text{flow}) - 0.001086(\text{DST}) + 0.001809(\text{duNouy}) \ldots\ldots \quad (7)$$

The r^2 for this correlation was 0.904. Table 2 lists the pertinent statistical information. This correlation shows K_La is well predicted by the chosen parameters.

K_L versus DST

The opaque aeration vessel used for K_La determinations prohibited the simultaneous determination of bubble radii during the unsteady state aeration tests. In order to determine size, bubbles were photographed at the same gas flow rate and liquid depth in a clear acrylic column, different in geometry and size than the aeration vessel. This modification in experiment technique required that X, γ, and K_La be averaged for each air flow rate and surfactant concentration; therefore, K_L's were calculated using the average bubble radii. This data reduction was necessary because no other practical alternative was available.

The bubble size and terminal rise velocity were used to calculate retention times. For the 20 L/min flow rate, bubbles were entrained by the turbulence,

TABLE 2. K_La as Function of DST, du Nouy, and Gas Flow Rates

Variable (1)	Parameter estimate (2)	Standard error (3)	t for H_0 (4)	Probability $\geq t$ (5)
Intercept	0.01732	0.011925	1.452	0.1511
Flow	0.0009144	0.0001068	8.56	0.0001
DST	−0.001086	0.0001863	−5.832	0.0001
du Nouy	0.001889	0.00008122	23.26	0.0001

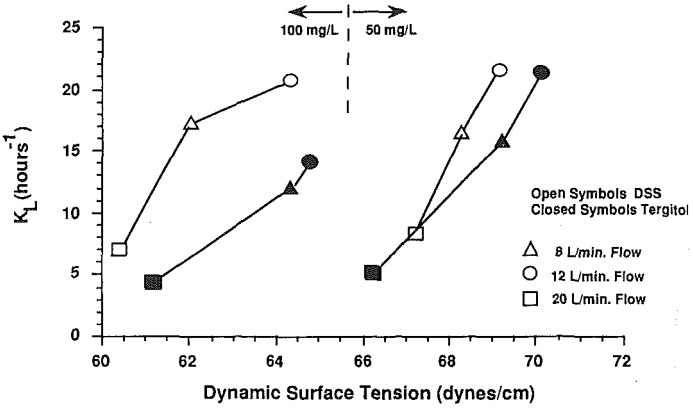

FIG. 13. K_L versus DST for Different Flows and Concentrations

forcing them downward and lengthening their retention times; therefore, the calculated retentions times doubled. With longer retention times, the surface area ages with more surfactants adsorbing at the interface producing a hydrolayer reducing surface renewal and decreasing K_L. Whereas faster water currents generated by the diffuser implies the bubble retention times should be shorter, the countercurrents of the short aeration column entrained bubbles. This was observed more emphatically at the 20 L/min air flow rate than at any other flow rate. The low K_L values of tap water confirms this decrease. Although K_L is reduced at 20 L/min, K_La is high; the large increase in transfer area more than compensates for the decrease in K_L.

The Tergitol data in Fig. 13 are represented by the filled symbols and the DSS data by open symbols. Both lie in relatively straight lines as a function of concentration. The high surfactant concentration has lower DST values than the lower surfactant concentration, at each flow rate, as expected from previous discussions. The K_L values at each flow rate for the high surfactant concentration are also lower than K_L for the lower surfactant concentration, as previously observed since more surfactants have the opportunity to adsorb onto the interface and reduce K_L.

Note the highest DST value corresponds to the highest K_L value. High DST values imply that less surfactants adsorb at the interface to inhibit mass transfer; therefore, K_L should be higher. The opposite is observed at the low DST and correspondingly low K_L readings. From the linearity of the lines and the similarity of the slope, it appears K_L can be predicted for these conditions.

CONCLUSIONS

This research correlated the volumetric mass transfer coefficient, K_La, and the liquid film coefficient, K_L, with dynamic surface tension (DST). This new water quality indicator, along with other measurable aeration parameters, allows for the rapid estimation of K_La and K_L in the presence of surface active agents, and also may facilitate using surface renewal theory in describing K_L. The mathematical model developed herein describes the DST

versus bubble life. The slope parameter, X, correlated to surfactant concentrations.

The aeration tests showed K_La was reduced in the presence of surfactants with larger decreases in K_La occurring with higher surfactant concentrations. The aeration tests also confirmed high X values corresponded to higher surfactant concentrations. The X value in aerated solutions had a larger variance than the X values in nonaerated solutions, suggesting that turbulence may cause surfactant gradients. A linear model relating K_La to DST, aeration flow rate, and the du Nouy measurement was formulated and had a high degree of fit ($r^2 = 0.904$).

Repeated unsteady state surfactant aeration testing showed K_La increased as the number of experiments on the sample solution increased. In general, X decreased with each experiment, suggesting surfactants deteriorated or were lost from the system. After a few aeration experiments on a surfactant solution, the foam changed from light and airy to dense and compact. Fresh surfactant solutions should be used during unsteady-state experiments.

The effect of an antifoaming agent was tested on these solutions. A small quantity of antifoam agent added to the solution dissipated the foam and produced a significant drop in K_La. This result stresses the need for care when using antifoam.

Film coefficients K_L were estimated for a series of experiments over a range of concentrations and flow rates. High DST values, indicating incomplete surfactant adsorption, were associated with high K_L values.

This research showed the DST measurement is a potentially useful and effective water quality indicator. A high DST or low X value indicates surfactant adsorption is low and mass transfer coefficients are high. K_L and K_La can be estimated from aeration parameters, surfactant concentration, and the DST value. In particular, DST measurements may eventually reduce reliance on empirical α factor testing. Although more testing and further research are required to strengthen the correlations, the DST parameter has the potential of becoming a major water-quality indicator.

APPENDIX. REFERENCES

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