The Effect of Surface Active Agents on Oxygen Transfer

by

Hyung Joo Hwang

Graduate Research Engineer

and

Michael K. Stenstrom

Principal Investigator and Assistant Professor

June 1979

Water Resources Program
School of Engineering and Applied Science
University of California, Los Angeles
Los Angeles, California

ACKNOWLEDGMENT

The research leading to this report was supported by the University of California Academic Senate, Los Angeles Division, under Grant No. 3453.

Abstract

The effects of Anionic Surface Active Agent (Dodecyl Sodium Sulfate) on oxygen transfer have been studied. Aqueous solutions containing 0 to 15 mg/l of DSS were tested with non-steady state technique using three different aeration methods: surface aeration, diffused aeration, and turbine aeration.

Results indicate that the presence of DSS significantly affects the oxygen transfer rate in all three cases depending on the DSS concentrations and power input. The effects of DSS were found to be similar for surface and turbine aeration, i.e., 5 mg/l of DSS reduced the apparent volumetric transport coefficients to 60% and 70% for surface and turbine aeration, respectively, at low power input. As power input increases, the effects of DSS on oxygen transfer are gradually decreased for both cases and approached and even exceeded unity. In diffused aeration, it was found that transport coefficients vary with 1.85 power of the ratio of the surface tension of wastewater to that of tap water.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER I

INTRODUCTION

The increasing consumption of synthetic detergent by daily household routines and industrial processes causes high concentrations in the influent to wastewater treatment plants. The presence of synthetic detergents and their effect on the efficiency of wastewater treatment processes, especially biological oxidation, has been a subject of major investigation. Biological oxidation is the most common secondary process, and aeration is the most energy-intensive operation. The recent increased energy cost requires more efficient aeration systems and a more fundamental understanding of the phenomenon of oxygen transfer.

Aeration methods can be classified basically into two categories: mechanical aeration and diffused aeration (1). The mechanical aeration method requires mechanical agitation of the water so as to promote the dissolution of oxygen from the atmosphere into the water. The two types of mechanical aeration commonly used are surface aeration and turbine aeration. In surface aeration, water droplets are splashed into the air, and some air bubbles are entrapped at the surface. Thus oxygen is entrained from the atmosphere. In turbine aeration, air is introduced in the bottom of the tank as coarse bubbles. These coarse bubbles are then split by rotating blades. In diffused aeration, air is introduced into the tank bottom to produce either fine or coarse bubbles.

The effects of surface active agents (SAA) on oxygen transfer to water have been studied by many investigators, but their observations and conclusions have not resulted in a consensus agreement. Some investigators have reported that the presence of SAA increases the oxygen transfer rate (2,3), while others have reported that it decreases the oxygen transfer rate (2,4,5), or produces only insignificant effects (37).

These different observations are believed to be due to the different conditions encountered for the various experiments, such as aeration method, SAA type and concentration, power input, etc.

For this study, non-steady state technique is used in tap water employing three aeration methods. The concentrations of SAA are varied from zero to 15 mg/l and power inputs are tested over a wide range.

The non-steady state technique involves deoxygenating the water in aeration vessel by addition of sodium sulfite catalyzed by cobalt ion. The deoxygenated water is then reaerated by various devices until the water becomes saturated with dissolved oxygen. The dissolved oxygen concentration is continuously recorded using DO probes, and the concentration vs. time data are used to estimate parameters with aid of computer.

CHAPTER II

LITERATURE REVIEW

A. THEORY OF OXYGEN TRANSFER

A-1. TWO-FILM THEORY.

Several theories for transfer of a gas to a liquid have been developed, but the best-known and most widely used theory is the two-film theory developed by Lewis and Whitman in 1924 (6). The basic concept of this theory is the existence of a thin gas film on the gas side of the interface and a thin liquid film on the liquid side of the inter face between the gas and liquid. For a gas to dissolve into the liquid, it must pass through those two films by slow molecular diffusion. The concentration of dissolved gases at the liquid film interface is in equilibrium with the gas phase as defined by Henry's Law. The concentration of the bulk of the liquid beneath this film is maintained uniform at all points by turbulent mixing. The liquid film is free from turbulence and the transfer across the films is in a steady state condition. Any concentration can not be built up at the films under a steady-state condition, therefore the resistance to transfer of solutes at the gas and liquid films is considered in series.

In the case of a slightly soluble gas in a liquid, such as oxygen in water, transfer rate is controlled by the resistance in liquid film and can be expressed as:

$$\frac{dm}{dt} = K_L A\ (C_S - C_L) \tag{1}$$

where

m = mass of oxygen

K_L = liquid film coefficient

A = area normal to mass transfer

C_S = saturation dissolved oxygen concentration

C_L = dissolved oxygen concentration in liquid

Equation (1) divided by liquid volume gives concentration change with respect to time as follows:

$$\frac{dC}{dt} = K_L \cdot \frac{A}{V}\ (C_S - C_L) \tag{2}$$

$$= K_L a\ (C_S - C_L) \tag{3}$$

where

$K_L a$ = volumetric or overall mass transfer coefficient

A = area normal to transfer

The principal limitation of the two film theory is in the assumption of a steady-state condition in the stagnant film. Other theories have been proposed to handle the unsteady state problem.

A-2. PENETRATION THEORY

The steady state assumption in a liquid film in the two film theory is abandoned in penetration theory. Higbie (7) studied the liquid film resistance of sparingly soluble gas in water. His concept was that when the gas and liquid are brought into contact, the concentration of solute in liquid film is the same as that of the body of the liquid. At first, the gas penetrates the interface of the gas-liquid interface and the concentration gradient decreases with time to reach a steady state gradient. Gas transfer during this penetration period is significant when the period of contact between gas and liquid is not much longer than the penetration period.

The mathematical representation is given by Fick's Law as follows:

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} \tag{4}$$

where

D_L = diffusivity

and the initial and boundary conditions are:

$$\begin{aligned} C &= C_L, \quad x > 0, \quad t = 0 \\ C &= C_S, \quad x = 0, \quad t > 0 \\ C &= C_L, \quad x = \infty, \quad t > 0 \end{aligned} \tag{5}$$

Then the solution of equation of (4) is:

$$C = C_L + \frac{C_S - C_L}{\sqrt{\pi D_L t}} \cdot \int_x^\infty \exp\left(-\frac{x^2}{4D_L t}\right) dx \tag{6}$$

The amount of oxygen absorbed during time of exposure per unit area can be calculated as:

$$f = - D_L \cdot \frac{\partial C}{\partial x}\bigg|_{x=0} \tag{7}$$

and the result is:

$$f = 2\sqrt{\frac{D_L \phi}{\pi}}\,(C_S - C_L) \tag{8}$$

then the gas transfer rate per unit time and unit area:

$$R_o = \frac{f}{\phi} = 2\sqrt{\frac{D_L}{\pi \phi}}\,(C_S - C_L) \tag{9}$$

and

$$K_L = 2\sqrt{\frac{D_L}{\pi \phi}} \tag{10}$$

where

f = mass transfer during time of exposure per unit surface area

R_o = mass transfer rate per unit time and unit surface area

ϕ = time of exposure

A-3. SURFACE RENEWAL THEORY

Penetration theory is based on concepts requiring the same exposure times of stagnant film. Danckwerts questioned the assumption of a stagnant film of liquid at the interface and suggested surface renewal theory (8). He assumed that the turbulence of liquid extents to the surface and replaces with fresh surface those older parts that have been exposed for a finite length of time. He derived the following expression:

$$K_L = \sqrt{D_L r} \tag{11}$$

where r = average frequency at which any particular vertical element is mixed

A-4. SUMMARY

Other theories have been proposed in addition to those previously mentioned (9,36). However, the main limitation for application of all theories using K_L independently of area is the difficulty in determining accurate surface area. Thus, the two film theory which uses K_L and A/V together in the form of an overall mass transfer coefficient has the advantage over other theories and is used frequently.

B. SURFACE ACTIVE AGENTS

B-1. CLASS OF SURFACE ACTIVE AGENTS

The widespread use of synthetic detergent has been a subject of major concern in the wastewater treatment field. Many studies have been done regarding the effects of Surface Active Agents (SAA) on the operation of the activated sludge process.

Chemically, there are two classes of surface active agents, the ionics and the non-ionics. The non-ionic surface active agents have non-ionizable hydrophilic end groups which contain a number of oxygen, nitrogen or sulfur ion in non-ionizing configurations. The ionic surface active agents have two divisions: cationics, in which an active portion or hydrophilic end is a cation, and anionics in which an active portion is an anion.

Another class of surface active agent, ampholytic, for example cetulaminoacetic acid, is not widely recognized as a separate class (11).

B-2. SURFACE ACTIVE AGENTS IN WASTEWATER.

Non-ionics are usually liquid or waxy in physical form and are not widely used (12). Cationics are also not widely used as detergents. Some cationics are used as effective germicides, but the amount is relatively small when compared to anionics. However, cationics react with anionics in sewage to form compounds which are neither detergents nor germicides. Since anionics are most widely used and the major portion of SAA in sewage, there is little need to comprise the effects of the cationics and non-ionics on wastewater treatment systems.

B-3. EFFECTS OF SURFACE ACTIVE AGENTS ON AERATION.

Many investigators have reported that the increasing concentration of surface active agents causes oxygen transfer coefficients to decrease (4, 5, 12-18), while other investigators have reported opposite results (2, 3, 19).

Surface active agents are considered to affect the oxygen transfer rate in two ways. Surface active agents in the bulk of water is adsorbed at the air-water interface and forms a film which offers additional resistance to mass transfer across the interface. Mancy and Okun (18) have found that the total resistance increases significantly under the presence of SAA at moderate mixing conditions.

Surface active agents also change hydrodynamic characteristics of water. It is usually considered that SAA increases the viscosity and depresses the hydrodynamic activity of the water, i.e. reduces surface tension (17).

It is very difficult to quantify the effects os SAA on mass transfer coefficients. Normally it is not possible to measure changes in K_L and area for commercially available aeration devices. Therefore, the alpha factor has been developed and is the commonly accepted method used to represent the variation of the rate of oxygen transfer due to water constituents. It is defined as the ratio of the oxygen transfer rate in wastewater to that in tap water, as follows:

$$\alpha = \frac{K_La \text{ wastewater}}{K_La \text{ tap water}} \qquad (12)$$

The variation of alpha caused by SAA depends on several factors, including SAA type and concentration (2,5,14,18), aeration method (2,4,18), degree of turbulence (14,21).

Baars (2) studied the effects of three types of anionics, Alkylsulphate, Alkylarylsulphonate and Lissapol. His results revealed that α decreases to 0.888 and 0.566 with 4 ppm and 10 ppm of Alkylarylsulphonate, respectively, while it decreased to 0.869 and 0.533 in the same concentrations of Alkylsulphonate. The effects of Alkylsulphate and Alkylarylsulphonate seem to produce the same change in alpha, but when 10 mg/l of Lissapol was tested, α decreased to 0.426. Apparently different types of SAA may develop different film characteristics in air-water interfaces, such as excess surface concentration, surface tension, and other phenomena.

Mancy and Okun (18) have reported that K_La drops to a minimum when the concentration of Aerosol O.T. is 20 mg/l, which is the critical micelle concentration of Aerosol O.T. After 20 mg/l of concentration, the further increase of Aerosol O.T. results in a gradual recovery of K_La. The extent of the recovery depends on the oxygen flow rate.

The variance of α depends also on aeration methods. In the same concentrations of Alkylarylsulphonate, α increased to about 1.8 using a brush aerator (2). This has also been observed by other investigators. In diffused aeration systems, α values are usually less than unity (22,23), and in surface aeration systems, α can be either greater or less than unity (2,5).

Another factor affecting the rate of oxygen transfer is the degree of turbulence. Otoski et. al. (3), using a static aerator, found that α is greater than one for high mixing levels and less than one for low mixing levels. Eckenfelder and Ford (25) reported three conditions of turbulence; under laminar consitions, there is substantially no effect on α ; under moderately turbulent conditions, a maximum depression in α relative to the concentration of SAA present occurs; at high degrees of turbulence, α approaches and exceeds unity due to increasing values of A/V in equation (2). Reported α values are summarized in table (1).

In diffused aeration system, the bubble size and shape are also important factors affecting K_La. Haberman and Morton found that the size and shape of the bubble can be related as follows (34):

if Re $\leq$ 300, spherical bubbles acting as rigid spheres rise with a rectilinear or helical motion, if $300 \leq Re \leq 4{,}000$, bubbles rise with a rectilinear, rocking motion,

if $Re \geq 4{,}000$, bubbles form spherical caps,

where

$$Re = \frac{\rho v d}{\mu} \text{ , Reynolds Number} \qquad (13)$$

ρ = density

v = bubble rising velocity

d = bubble diameter

μ = dynamic viscosity

Barnhart (10) studied the effects of bubble size on K_La, and he concluded that K_La is optimum at a bubble diameter of 0.22 cm.

It is therefore hypothesized that:

1) for diffused aeration systems, α decreases with concentration of SAA but it is not affected much by the degree of turbulence.

2) for mechanical aeration systems, in addition to the type and concentration of SAA, the degree of turbulence also affects α.

Table 1. Variation of α Values with Water Contents and Aetation Methods.

Aeration Method	Water Contents		References
Kessener Brusher	Sterilized Sewage	0.82	26
Compressed Air	"	0.2	26
Fine Bubble Diffuser	20 - 100 mg/l SAA	0.5	21
Disc Surface Aerator	"	0.8	21
Fine Bubble Diffuser	4 - 10 mg/l SAA	0.9 - 0.4	2
"	4 - 10 mg/l AFA	0.8 - 0.85	2
Kessener Brusher	"	2.	2
Searle Aerator	10 mg/l ABS	2.	4
Simple Cone Aerator	"	1.1 - 1.15	4
Static Mixer	for high mixing level	1	3
"	for low mixing level	1	3
Diffused Aerator	Waste from an Organic Chemical Plant	0.73-0.83	23

Table 1. continued

Surface Aerator	Waste from an Organic Chemical Plant	0.69-0.78	23
Surface Aerator	Mixed Liquor	0.78-0.99	20
Capillary Tube	20 - 40 mg/l Aerosol O.T.	0.4	17
Bubble Aerator	10 mg/l SAA	0.37	18
"	300 mg/l SAA	0.65	18

C. MODELS FOR OXYGEN TRANSFER AND PARAMETER ESTIMATION

Many mathematical models have been developed to determine the parameters needed to estimate oxygen transfer in water, and most are based on the two-film theory. Although the penetration theory or surface renewal theory has some advantages for estimation of an accurate liquid film coefficient, because of difficulties regarding the determination of interfacial area, they are not used as often as the two-film theory.

In equation (2), the saturation concentration of dissolved oxygen is not constant and varies with hydrostatic head, partial pressure of oxygen in gas phase, and the constituents of water. Therefore equation (2) must be rewritten with a new set of parameters, as follows:

$$\frac{dC}{dt} = K_La^*(C_S^* - C) \qquad (14)$$

where

K_La^* = apparant volumetric transport coefficient.

C_S^* = apparant saturation concentration of dissolved oxygen.

The non-steady state technique is a commonly used technique to evaluate the parameters in equation(14). This technique involves deoxygenation of the water in aeration vessel by addition of sodium sulfite. Sodium sulfite is used in excess amount of stoichiometric amounts, catalyzed by cobalt sodium to ensure complete deoxygenation. The water is then reoxygenated by various devices until the water becomes saturated with dissolved oxygen and the DO concentration vs. time is continuously recorded using DO meters and a recorder.

Using the data collected in non-steady state reaeration tests, the parameters in equation (14) can be estimated.

There are three commonly used methods for estimating K_La^*: log-deficit, differential, and exponential methods (30). The methods can be further regimed based upon the method of estimating C_S^*:

1) Calculation of the value of C_S^* from handbook values (27,28,29) of C_S using corrections for diffuser submergence.

2) Measurement of equilibrium value if C_S^* in non-steady state test.

3) Estimation of C_S^* from the data by a parameter estimation technique.

Three techniques were used in this investigation; differential model, log deficit model and exponential model.

C-1. DIFFERENTIAL MODEL

Equation (14) can be rearranged so as to use linear regression method for the differential model (31,34).

$$\frac{dC}{dt} = K_La^* \cdot C_S^* - K_La^* \cdot C \qquad (15)$$

The assumptions in this model are:

1) The errors in measuring the dependent variable $(\frac{dC}{dt})$ are uniform with a mean of zero.

2) No error is associated with measurement of the independent variable (C).

C-2. LOGARITHMIC MODEL.

Equation (14) can be integrated from zero to t, and rearranged to produce the logarithmic form as follows:

$$\ln(C_S^* - C) = -K_La^* t + \ln(C_S^* - C_i) \qquad (16)$$

The parameters K_La^* and C_S^* can be calculated by a non-linear regression technique or by an iterative linear regression, over a range of trial values.

Since the experimental error in measuring the concentration is normally distributed with mean zero, a value of C greater than C_S^* can be measured. Therefore this model requires the truncation of test data near saturation to avoid taking the logarithm of a negative number.

C-3. EXPONENTIAL MODEL.

Equation (16) can be rearranged as follows:

$$C = C_S^* - (C_S^* - C_i) \cdot \exp(-K_La^* \cdot t) \qquad (17)$$

and the parameter can be obtained by a non-linear regression technique.

It has been reported that the exponential model does not require data truncation and provides the most precise estimation of K_La^* and C_S^*. The differential method provides the least precise estimate of C_S^* and K_La^*, and the log deficit method provides biased estimates (30).

For the parameter estimation in this study, the exponential model was applied for all experimental data.

Equation (17) is a non-linear equation with respect to

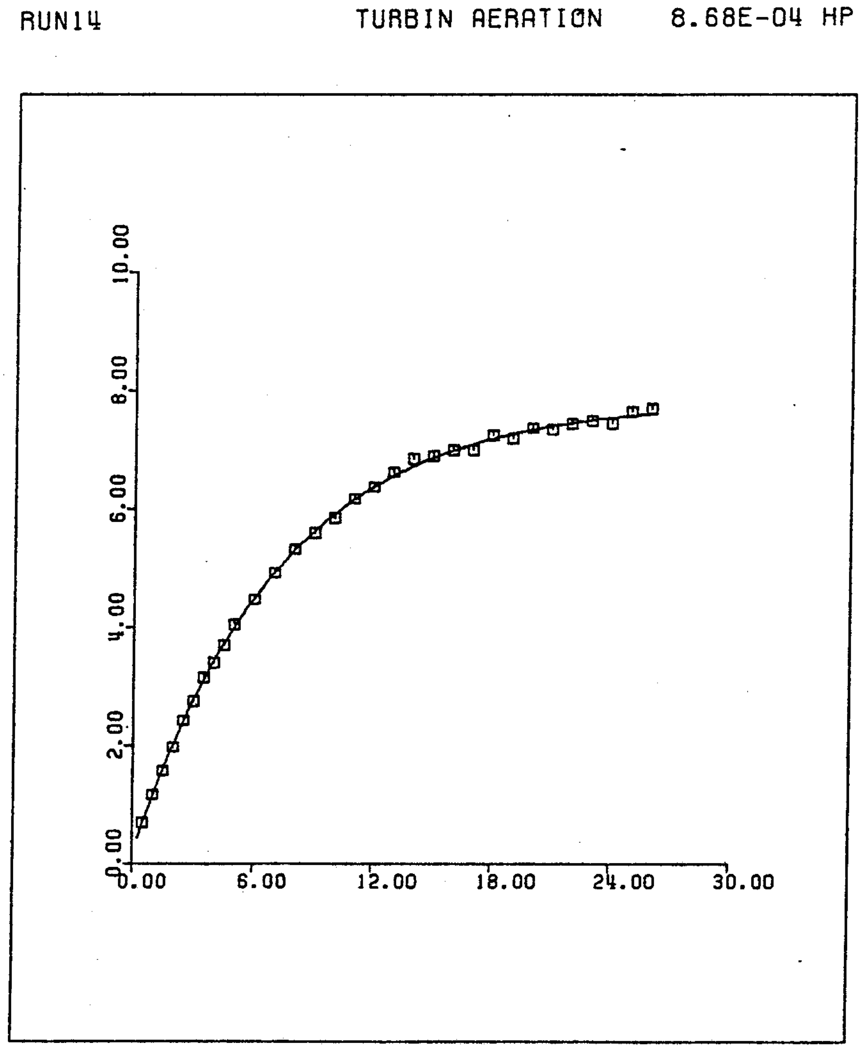


Figure 1-a. Data Fitting with Exponential Model.

parameters K_La^*, C_S^* and C_i, and the objective function for non-linear regression can be written as:

$$\min_{K_La^*, C_S^*, C_i} \sum \left\{ C - C_S^* + (C_S^* - C_i)\exp(-K_La^* \cdot t) \right\} \tag{18}$$

Average values of dissolved concentration from two probes at time t were used in equation (18) to evaluate parameters.

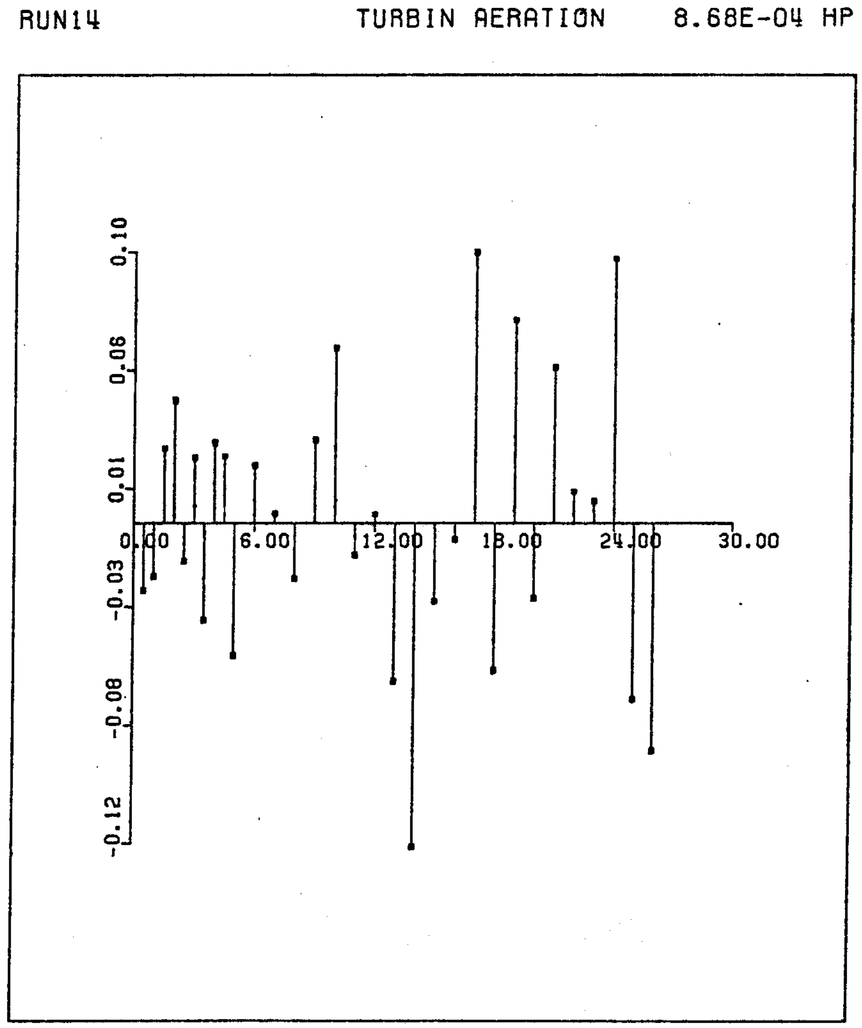


Figure 1-b. Residual Plot for Exponential Model.

CHAPTER III

EXPERIMENTAL SET-UP AND PROCEDURE

A. AERATION EQUIPMENT.

The aeration system consisted of a plastic circular tank of 55-gallon capacity shown in figure (2). Four baffles, each one-tenth of the tank diameter and full water depth, were placed around the tank circumference at the wall. Aeration was provided using three different methods.

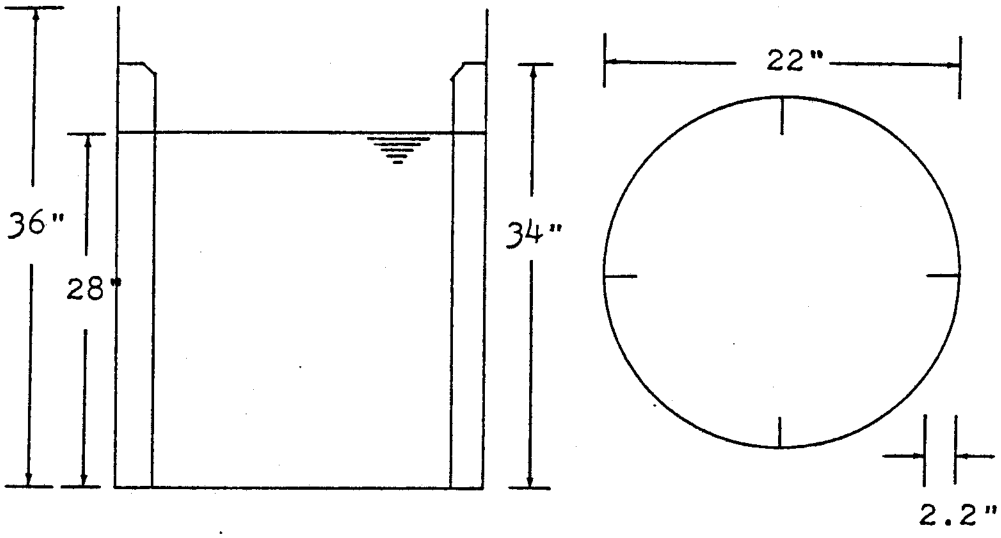


Figure 2. Geometry of 55-gal Aeration Vessel.

A-1. SURFACE AERATION.

For surface aeration, 3-bladed impellers were used in 3 different diameter sized: 2, 3 and 3.5 inches. The drive system (Cole Parmer) consists of two parts: a permanent magnetic DC-motor-generator and a solid state electronic controller. The motor provides an output torque to drive the impeller and the generator provides a feedback signal to the controller, which compares this signal to an internal reference value and adjusts the current supply in order to maintain a constant speed. The controller can simultaneously measure both the rotational velocity of the impeller in RPM, and the torque imposed on the impeller by the liquid and indicates by a millivolt meter. The millivolt signal is converted to torque through the calibration chart or a linear

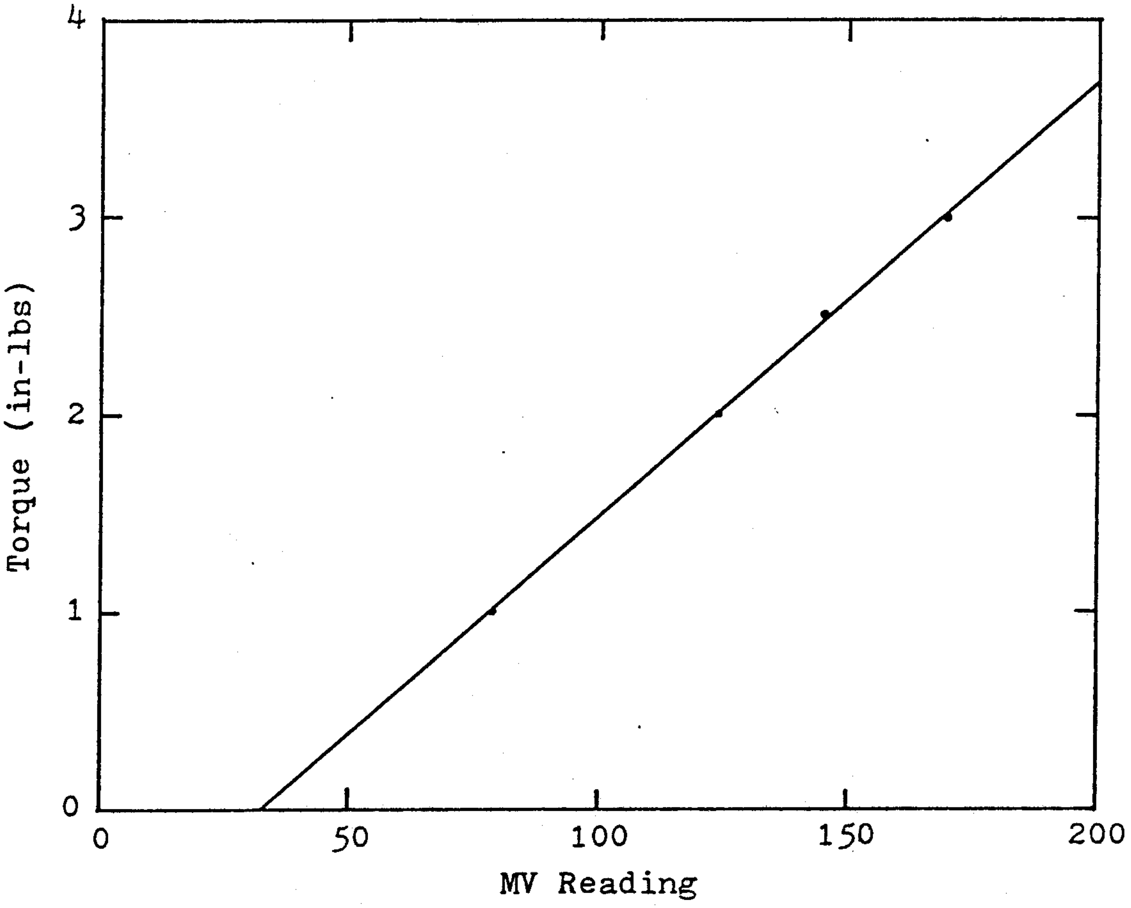


Figure 3. Calibration Chart for Motor-Controller.

equation derived from the chart of figure (3)

The power consumption for aeration can be calculated by the following equation.

$$HP_r = \frac{dW}{dt} = L \cdot \omega \tag{19}$$

$$= L \cdot \omega \cdot \frac{1}{12} \cdot \frac{1}{60} \cdot \frac{1}{550}$$

where

HP_r = impeller power consumption

W = energy

L = torque imposed on impeller

ω = rotational velocity

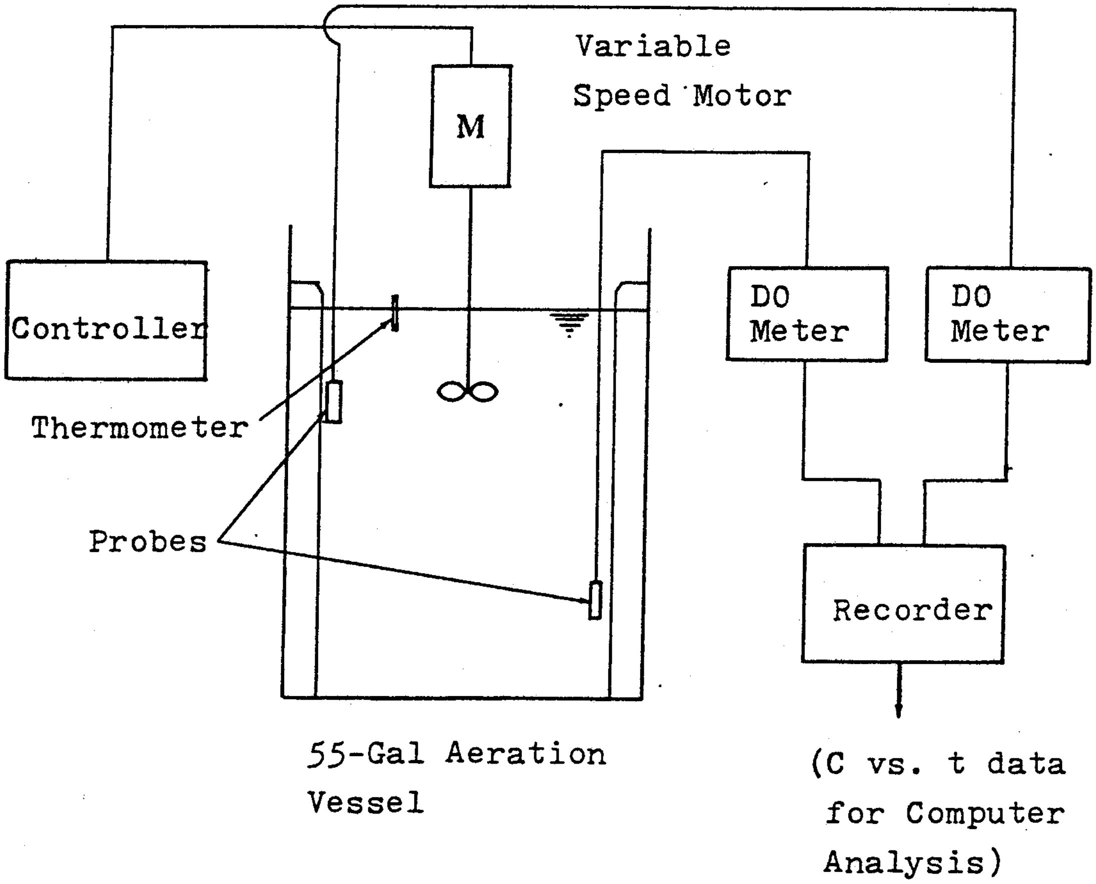


Figure 4. Experimental Set-Up for Surface Aeration

A-3. DIFFUSED AERATION.

Two fine bubble diffusers were connected 5" apart and 2" from the tank bottom to give 26" submergence. Pressurized laboratory air was used and controlled by a valve attached to micrometer vernier. Flow rate was measured by a rotometer and pressure was measured by a mercury manometer as shown in figure (5). The flow meter reading was converted using the calibration chart provided by manufacturer to give the flow rate. For convenience, an equation was derived from the calibration chart for the range of 4,000 to 12,400 ml/min.

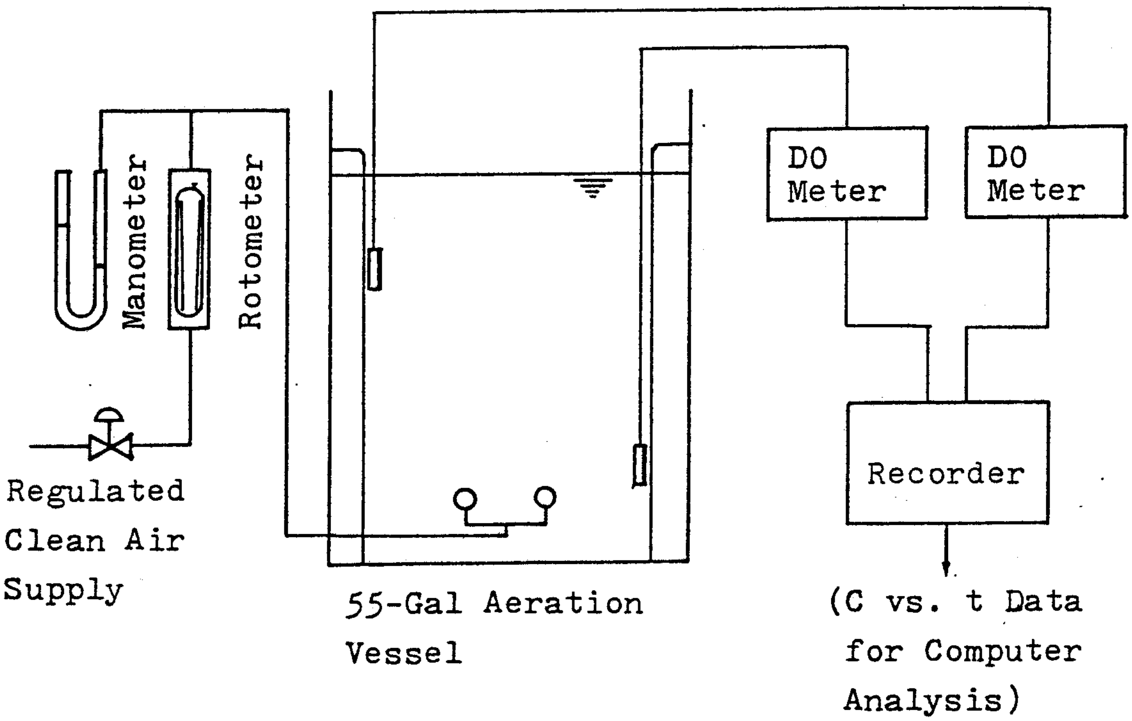


Figure 5. Experimental Set-Up for Diffused Aeration

To calculate Power consumption, the equation for adiabatic compression was applied (1).

$$HP_c = \frac{wRT}{550ne}\left[\left(\frac{P_2}{P_1}\right)^n - 1\right] \qquad (20)$$

where

HP_c = compressor power consumption

w = mass flow of air

R = gas constant

T = absolute inlet temperature

p_1 = absolute outlet pressure

p_2 = absolute outlet pressure

n = $(k-1)/k$, 0.283 for air

k = 1.395 for air

e = efficiency of compressor

After all constant values are applied, the equation (20) comes out:

$$HP_c = 1.5145 \times 10^{-8} \cdot F \cdot T \, \frac{76 + p^{0.283}}{76} \qquad (21)$$

where

F = air flow rate (ml/min)

T = absolute inlet temperature (^oR)

p = inlet pressure (cm-Hg)

A-3. TURBINE AERATION.

For turbine aeration, surface and diffused aeration systems were combined with a slight change. A coarse bubble diffuser made of brass was used instead of a fine bubble diffuser. The diffuser has four No. 33 hole openings (0.1130"). A 2.9 inch rotor was used for mixing. The clearance between the diffuser and the bottom was 2 inches to give 26 inch submergence and the distance between the rotor and diffuser varied from 2 inches to 4.5 inches. Figure (6) shows the experimental set-up.

A-4. SURFACE TENSION.

Surface tension was measured with the Fisher Surface Tensiomat, Model 21, which uses the du Nouy ring method. The platinum-iridium ring was cleaned by rinsing it in benzene and acetone, then heated in the oxidizing portion of a gas flame. The instrument shows the apparent surface tension which must be converted to absolute values by an appropriate factor according to the constant provided by the manufacturer.

Surface tensions for each concentration of DSS were predetermined before aeration experiment as shown in figure (7).

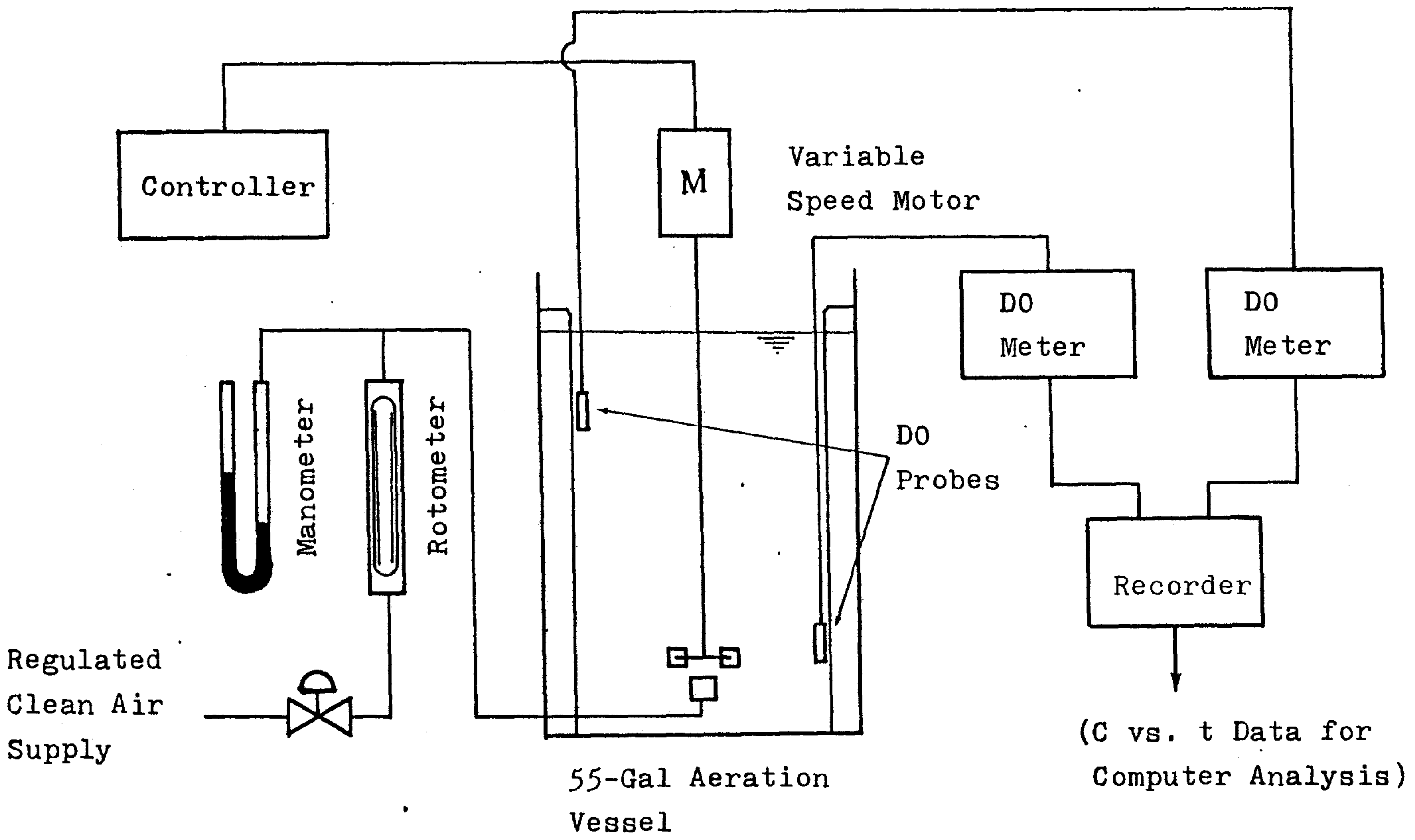
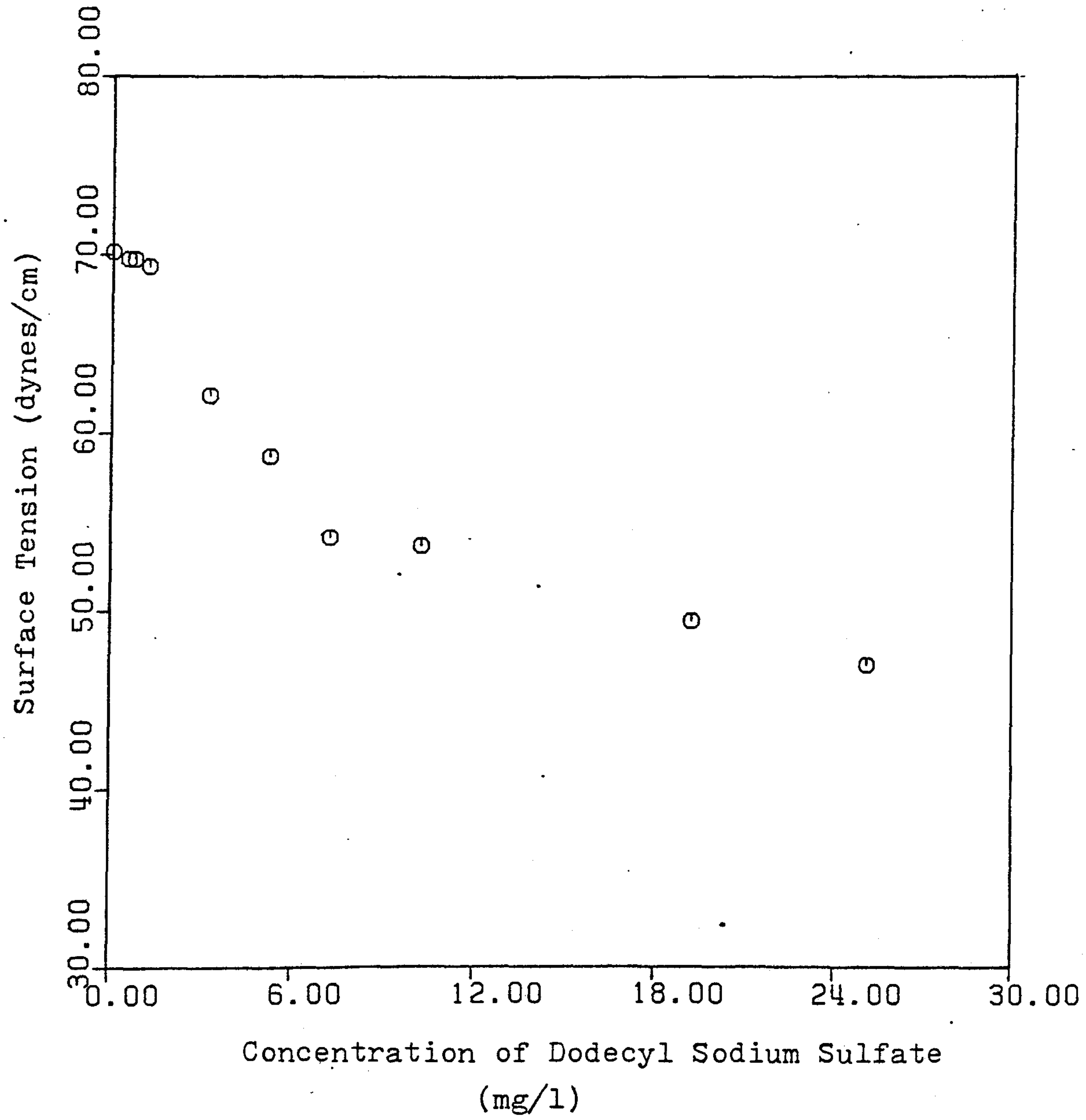


Figure 6. Experimental Set-Up for Turbine Aeration.

Figure 7. Surface Tension vs. Dodecyl Sodium Sulfate Concentration.



B. ANALYTICAL METHODS.

The dissolved oxygen concentration was monitored continuously using two membrane electrodes, YSI Model 5739 which were connected to YSI Dissolved Oxygen Meters, Model 51B. The manufacturer provides two thicknesses of membranes: standard and high sensitivity membranes (0.001 inch and 0.0005 inch respectively). The oxygen electrode can be modeled using the concept of an ideal electrode, with instantaneous responses, in series with a first order lag. The mathematical description is as follows:

$$\frac{dC_p}{dt} = \frac{(C - C_p)}{\tau} \tag{22}$$

where C = dissolved oxygen concentration at the probe surface

C_p = dissolved oxygen concentration indicated by the probe

τ = probe time constant

The thickness of the membrane determines the time constant, τ. For most work, the time constant is of very little importnace: however, for kinetics investigations, it has been shown (30) that an error in the estimation of K_La^* is produced if the time constant is large compared to K_La^*. To determine the effects of membrane thickness, a preliminary study in a 1,000 ml beaker with magnetic stirrer was performed and showed little difference in K_La^* for the different

Table 2. Comparison of High Sensitive Membrane and Standard Membrane.

Test Run	K_La^* (1/min)	
	High Sensitive Membrane	Standard Membrane
T-1	0.1071	0.1654
T-2	0.3285	0.3046
T-3	0.5414	0.5190
T-4	0.7205	0.7050
T-5	0.9916	0.9765
T-6	1.0540	1.0500
T-7	1.1122	1.0617

membranes, as shown in Table 2. The high sensitive membrane is very sensitive to fluctuations of the concentration of dissolved oxygen and to the turbulence in tank. In these series of experiments, a high sensitive membrane was used for 22 inch submergence probe and a standard membrane was used for 6 inch submergence probe.

The probes were calibrated regularly by the Azide Modification of the Winkler Titration Method (28). The dissolved oxygen meters were connected to recorders and the concentration vs. time was continuously recorded.

Each experiment was performed using the following procedure, which was modified from those instructions recommended by other investigators (32).

1. Wash the aeration tank with tap water for 4 to 5 hours (12 - 15 cycles)
2. Fill the tank with tap water to the desired volume.
3. Dissolve a proper amount of surface active agent in a 500 ml beaker and then mix it in the aeration tank.
4. Add cobalt chloride solution prepared so that 100 ml solution can produce 0.5 mg/l as cobalt ion in 45 gallon of water.
5. Dissolve sodium sulfite in 300 ml of tap water and pour it into the aeration tank. One and one fourth to one and one half the stoichiometric requirement of sodium sulfite was used.
6. Mix the water in the aeration tank with 2-inch propeller at 2400 rpm until all oxygen probes submerged at different locations become stabilized at zero mg/l of DO concentration.
7. Start aeration and record the DO concentration vs. time until the water becomes saturated with dissolved oxygen.

Water temperature varied from 24 to 30.5°C during the series of experiments. To compensate the effect of temperature on the oxygen transfer rate, 1.02 was applied as a "theta" value for all data. The theta factor is commonly defined as:

$$K_La_{20} = K_La_T \cdot \theta^{20-T} \qquad (23)$$

Table (3) shows variation of theta value, and 1.02 is the average value and is commonly accepted.

Table 3. Theta Values

Aeration Method	θ	References
Sparger and Saran Tube	1.09	22
Surface Aerator	1.03 for T 20°C	36
	1.01 for T 20°C	36
Bubble Diffuser	1.02	10,24,25

CHAPTER IV

RESULTS AND DISCUSSION

A. SURFACE AERATION.

In this study, Dodecyl Sodium Sulfate (DSS), which is an anionic surface active agent was used. Analytical reagent grade DSS was used. The concentrations was varied from zero to 15 mg/l, producing the surface tension range found in most domestic sewage.

In the surface aeration experiments, power inputs varying from 2.3×10^{-3} HP to 9.2×10^{-3} HP in 45 gallon of water (from 51 HP/MG) were studied.

Oxygen transfer rate was found to increase linearly with power input in tap water and the presence of SAA did not significantly affect this linear relationship. Using tap water containing 1 and 5 mg/l of DSS, at low power input of 3.5×10^{-3} HP, the K_La^*'s decreased to approximately 75% and 60% respectively of that in tap water alone. At a higher power input of 7.5×10^{-3} HP, the presence of DSS had no effect on K_La^* as shown in figure (8). If power input had been increased above 7.5×10^{-3} HP, K_La^* in DSS solution may have been greater than that in tap water.

The alpha factor vs. power for different DSS concentrations are plotted in figure (9). Since the value K_La^* varied linearly with power input for each DSS concentration the α factor can be related to the power input as follows:

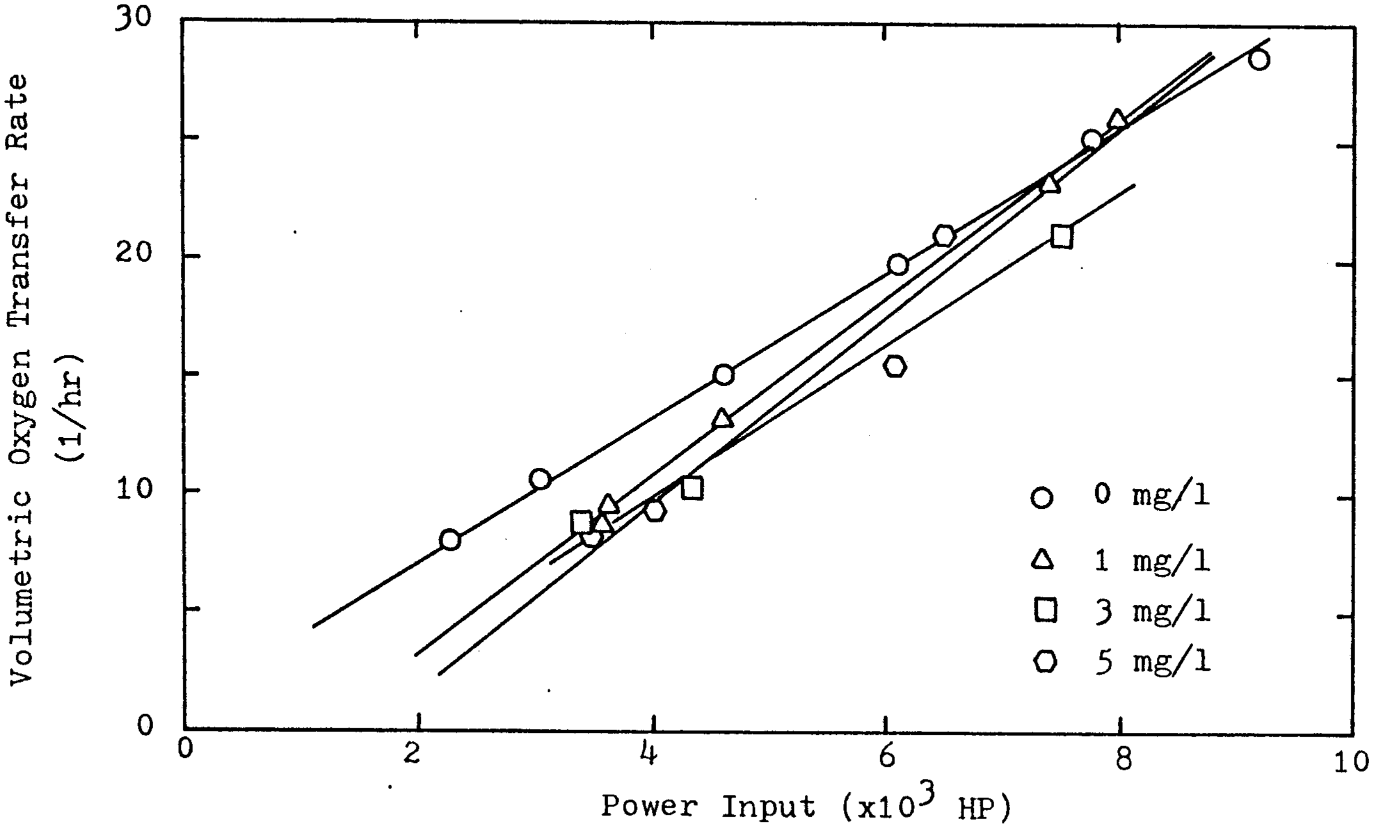


Figure 8. Volumetric Oxygen Transfer Rate vs. Power Input in a 55-gal. Vessel with Surface Aerator in the Presence of SAA.

$$\alpha = \frac{K_La_{wastewater}}{K_La_{tap\ water}}$$

$$= \frac{a_wP + b_w}{a_tP + b_t}$$

$$= \frac{A_w}{P + {}^{b}t/a_t} + B_w \qquad (24)$$

where

$$A_w = \frac{b_w}{a_t} - \frac{a_wb_t}{a_t^2}$$

and

$$B_w = \frac{a_w}{a_t}$$

where a,b,A,B = constants for a given concentration

subscripts w and t represents wastewater and tap water, respectively.

With equation (22), figure (9) was plotted. If the constants A_w and B_w can be expressed experimentally as a function of surface tension and viscosity, α can be estimated only with the data of tap water tests and a few measurable values.

In this series of aeration experiments, the DSS concentration could be varied from zero to 5 mg/l. In this range of concentration, flow patterns, as shown in figure (10-a), were fully developed in aeration tank. As the concentration of DSS increased above 5 mg/l, the circulation patterns changed to the form shown in figure (10-b). This change may be due to increased viscosity. Poor mixing results in a ununiform concentration distribution with respect to the location as shown in figure (11). This phenomenon has been observed in a full scale installation by Price, et al. (35).

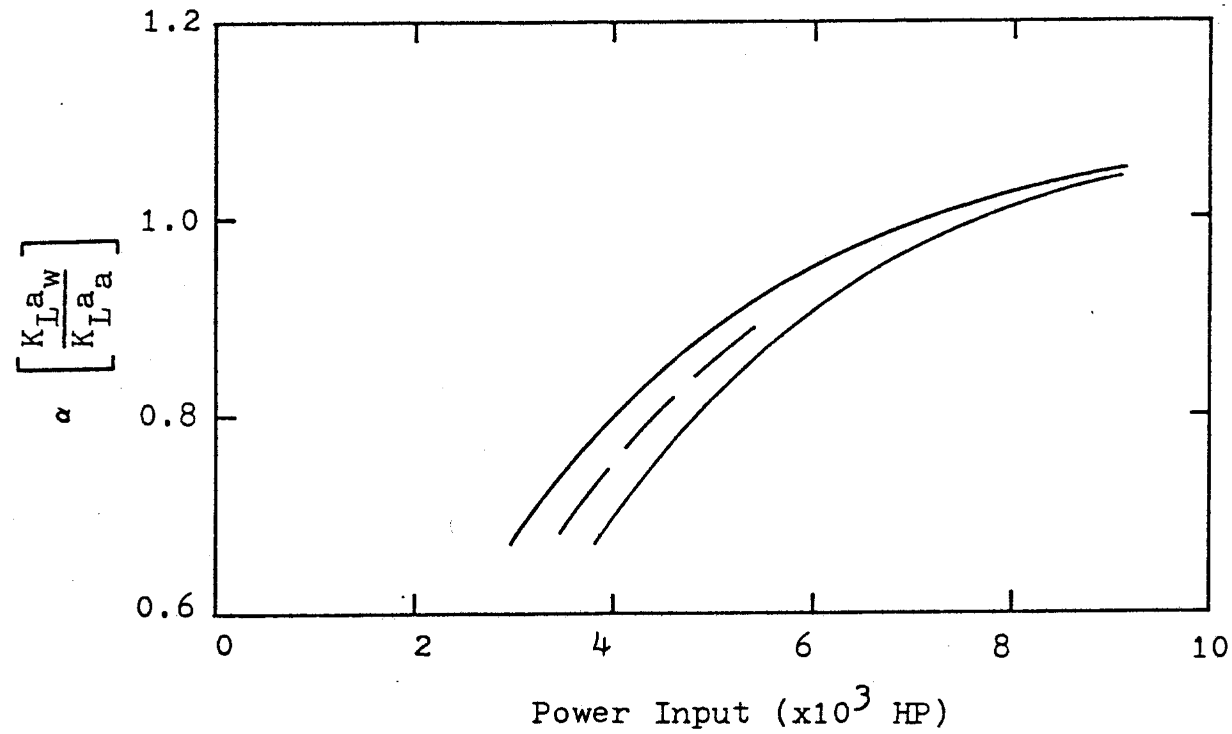
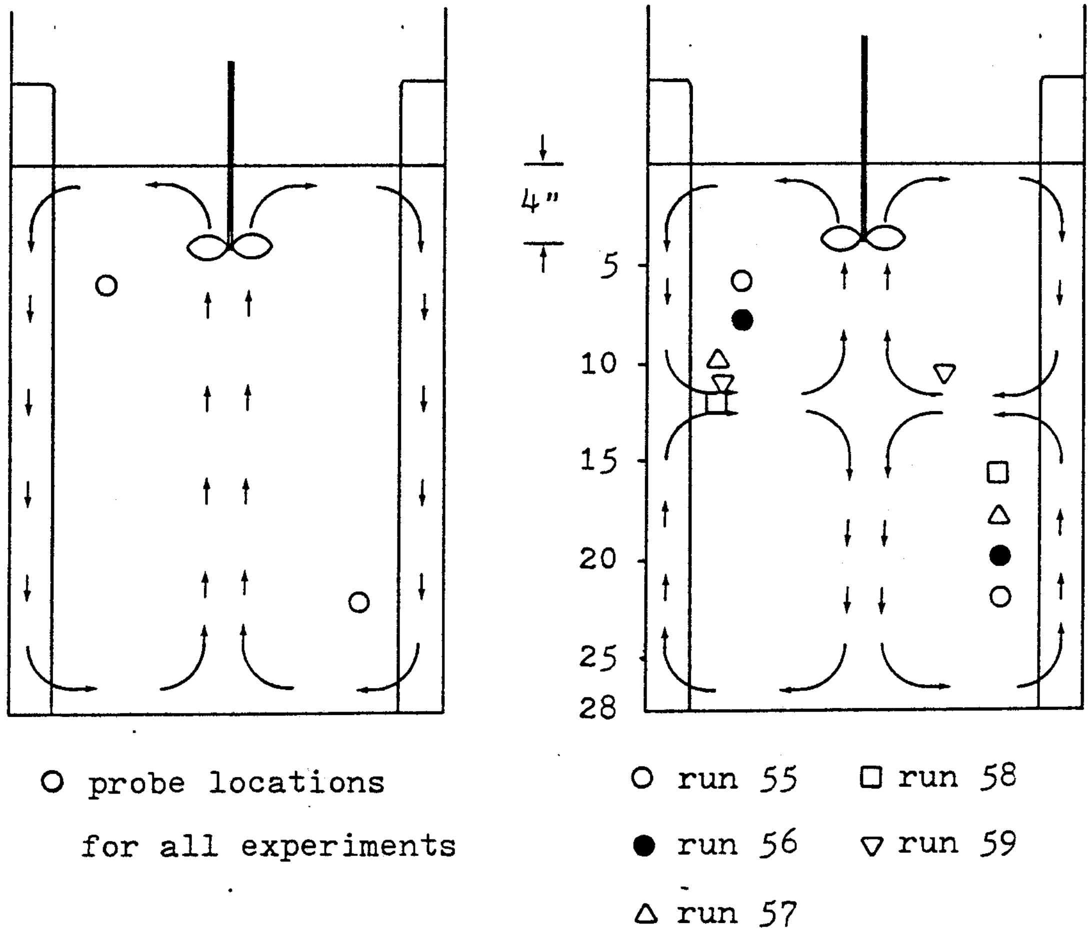


Figure 9. α vs. Power Input in Surface Aeration



(a) (b)

Figure 10. Flow Patterns in Aeration Tank Containing 0 and 15 mg/l of DSS Concentration.

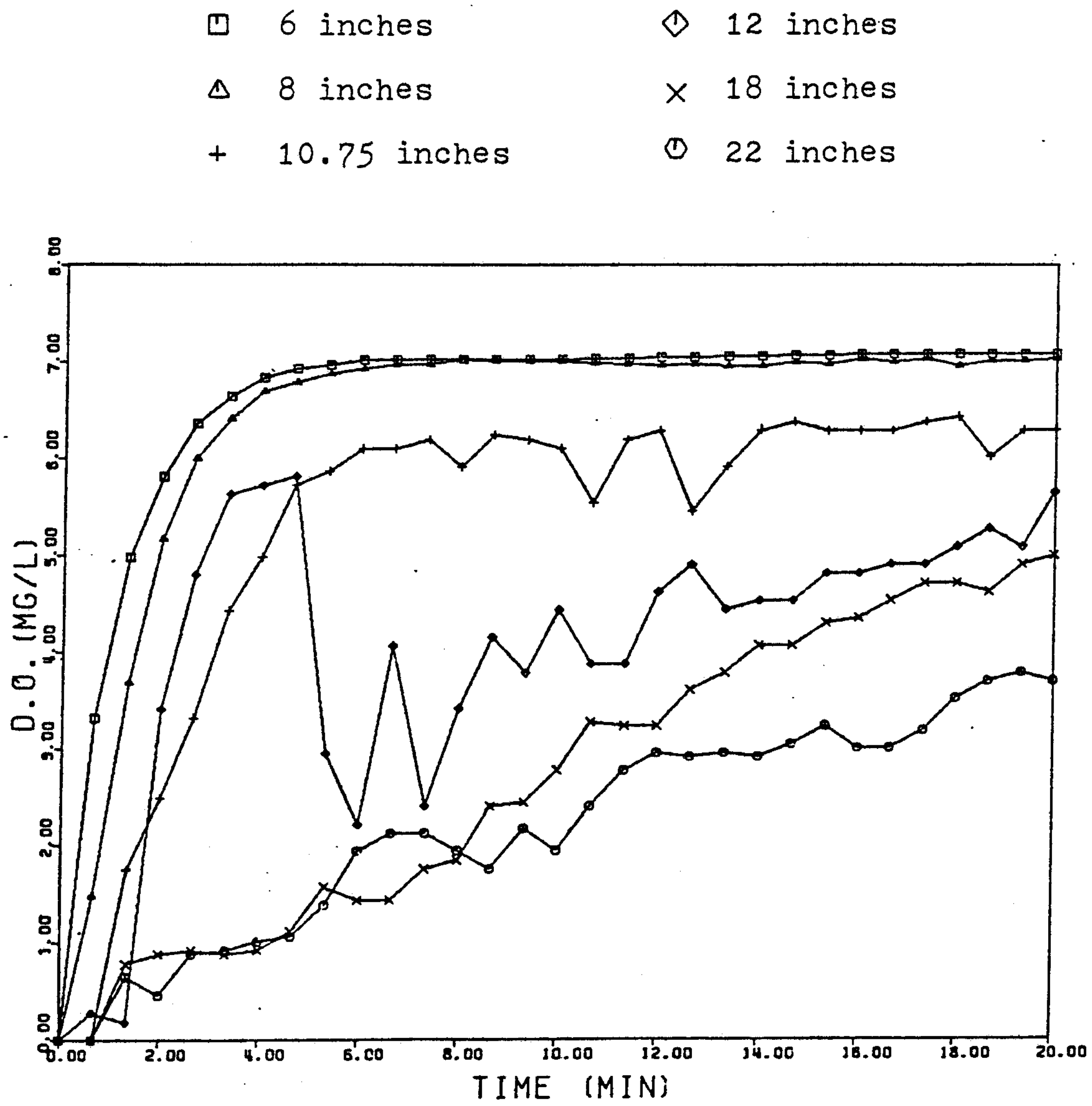


Figure 11. DO Concentration vs. Time at Various Depths with 15 mg/l of DSS.

B. DIFFUSED AERATION.

The power input varied from 3×10^{-3} HP to 4.5×10^{-3} HP (from 67 HP/MG to 100 HP/MG) which is a more restricted range than for surface aeration. Figure (12) shows the effects of DSS on K_La^*, which decreased as the concentration of DSS increased. When 1.0 and 15.0 mg/l of DSS were added to the aeration tank, then the resulting values of K_La^* were reduced to 98% and 55% respectively of that in tap water alone. From this result, K_La^* can be related to surface tension as:

$$K_La^*_w = K_La^*_t \left[\frac{\sigma_w}{\sigma_t}\right]^{1.85} \qquad (25)$$

This experimental equation gives a reasonable estimation of $K_La^*_w$ with about 10% of error in worst case. These errors are believed due to the change of kinematic viscosity of the water containing DSS (figure 13).

C. TURBINE AERATION

The turbine aeration experiments were performed in the power range of 2.0×10^{-3} HP to 3.5×10^{-3} HP (44 HP/MG to 78 HP/MG) and in the DSS concentration range of zero to 15 mg/l.

Eckenfelder and Ford (25) showed that the optimum oxygen transfer efficiency occurs when HP_c/HP_r is near 1.0. In the table presented in appendix, the HP_c/HP_r is 1.53

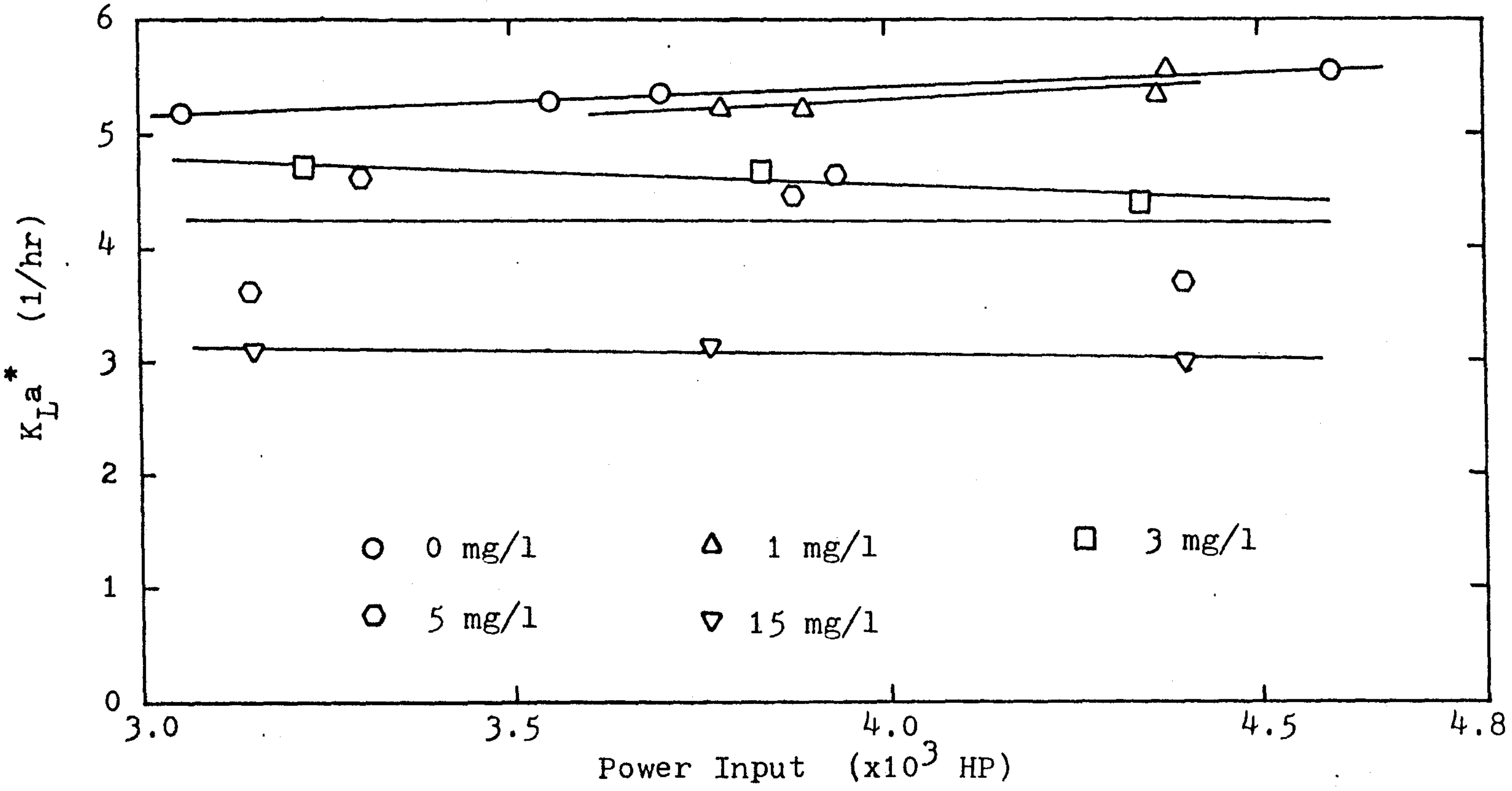


Figure 12. Apparent Volumetric Transport Coefficient vs. Power Input in Diffused Aeration.

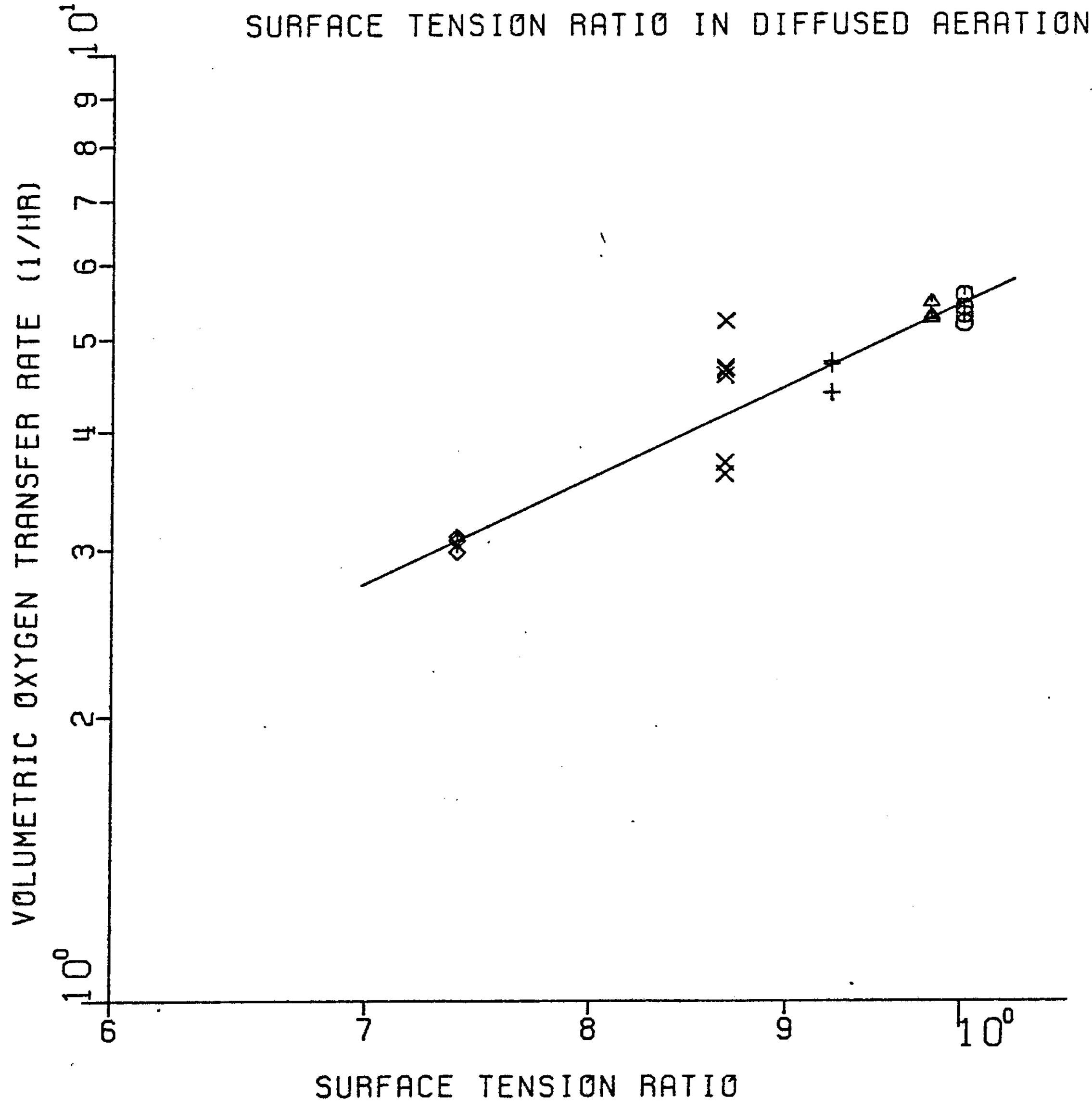


FIGURE 13. VOLUMETRIC OXYGEN TRANSFER RATE VS. SURFACE TENSION RATIO IN DIFFUSED AERATION

and 1.00 for run 14 and 46 respectively. While the total power input for run 14 is higher than that of run 46, run 14 gives a 20% lower value of K_La^* compared to run 46. Therefore the data with values of HP_c/HP_r close to 1.0 were used and reported for analysis.

Figure (15) shows the changing K_La^* values for the various DSS concentration. At low power inputs, the effects of DSS on K_La^* is pronounced. At power of $2.0x10^{-3}$ HP and varied DSS concentration of 1.3 and 5 mg/l, the respective K_La^* values, were found to decrease to 88.7%, 73% and 70% of that in tap water free of DSS. However, at a DSS concentration of 15 mg/l, the K_La^* value were found

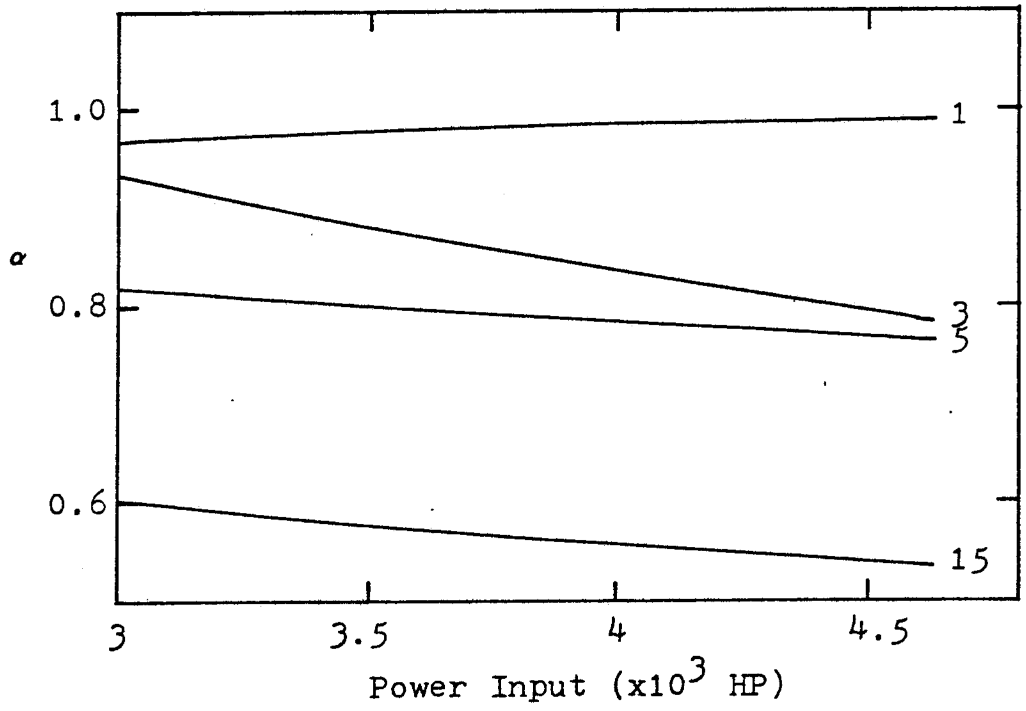


Figure 14. α vs. Power Input in Diffused Aeration

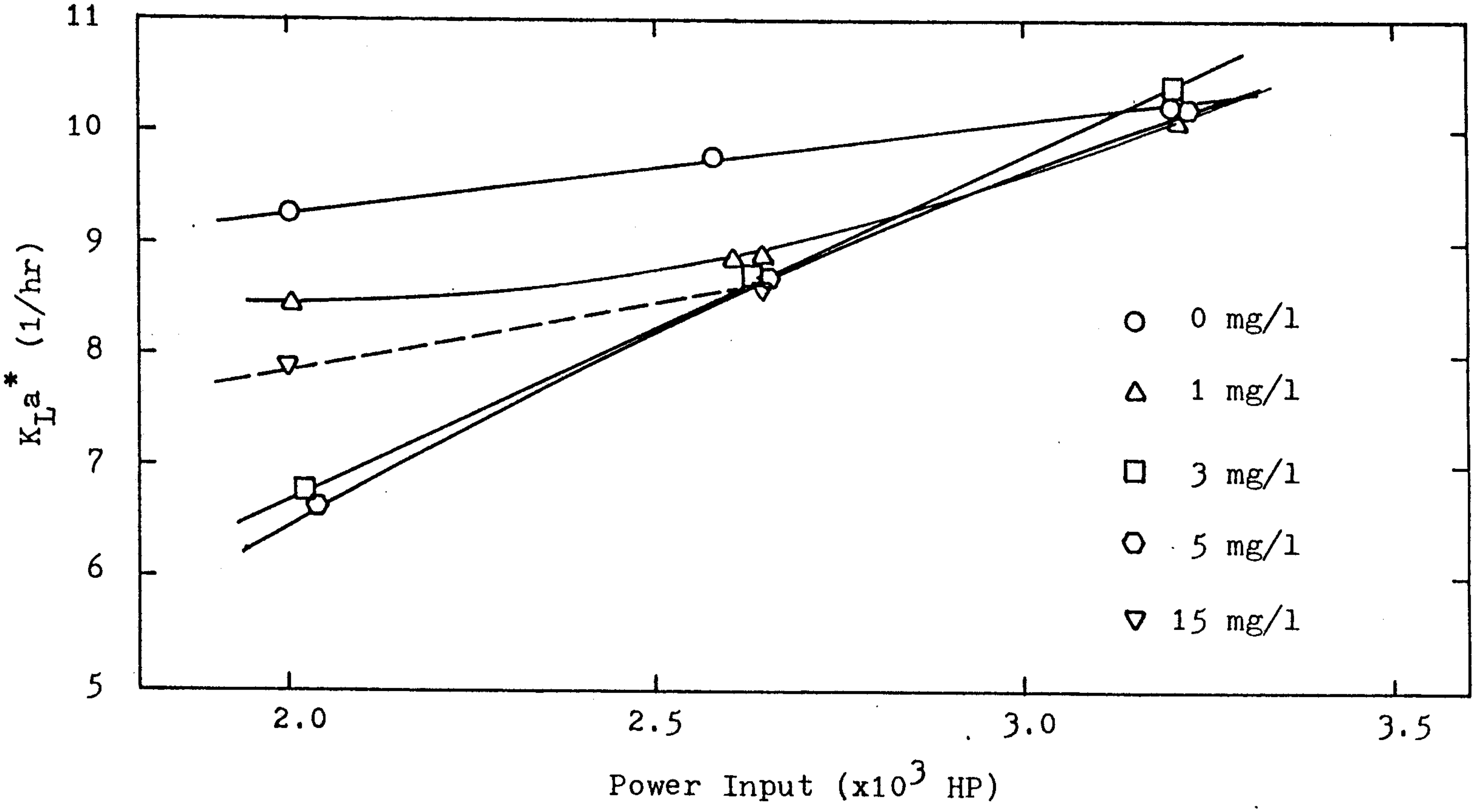


Figure 15. Apparent Volumetric Transport Coefficient vs. Power Input in Turbine Aeration.

to only decrease to 84% of K_La^* of tap water free of DSS.

As power input increases, the effect of DSS on oxygen transfer is gradually reduced so that at 3.2 x 10^{-3} HP power input, the K_La^*'s do not deviate over 5% from the value for tap water.

The value of K_La^* vs. power input for various concentration of DSS are plotted in figure (15).

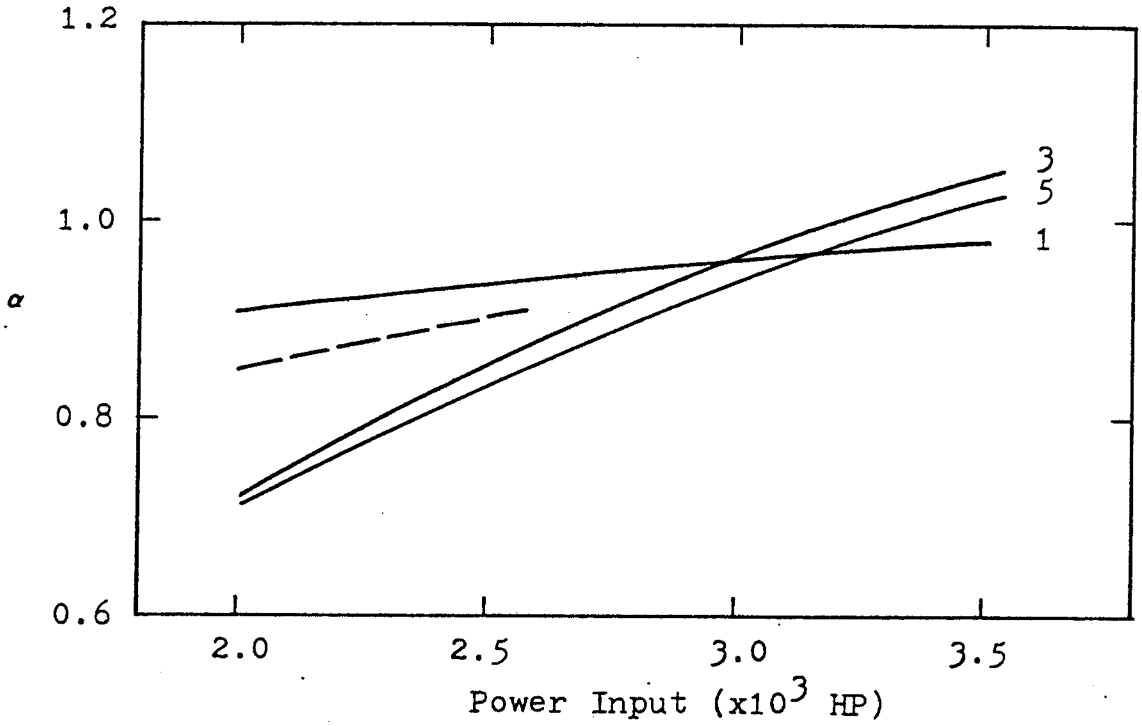


Figure 16. vs. Power Input in Turbine Aeration.

CHAPTER V

CONCLUSION

The effects of surface active agents on K_La^* and α are significant for all aeration methods used in this study. The presence of SAA in water reduces surface tension considerably and this decreasing surface tension directly affects the K_La^*.

The effects of SAA are similar for both surface aeration and turbine aeration. In the surface aeration test, 1 and 5 mg/l of DSS reduces $K_La^*_w$ from 11.5 hr^{-1} of tap water to 8.7 and 7.0 hr^{-1} respectively at 3.5×10^{-3} HP. When the power input is increased to 7.5×10^{-3} HP, the effects of SAA are reduced and K_La^*'s have a relatively constant value of 23.5 hr^{-1} with all SAA concentration.

In turbine aeration, at low power input of 2.0×10^{-3}HP, $K_La^*_w$ decreased rapidly with increasing SAA concentration up to 5 mg/l. However, at 15 mg/l of SAA, the K_La^* value increased again. At relatively high power input of 3.2×10^{-3} HP, SAA exerted no effect on K_La^*, and K_La^* remained a constant value for all concentration of SAA.

In diffused aeration, SAA has more significant effects on K_La^*. The value of K_La^* decreased remarkably with increasing DSS concentration for all levels of power input. It can be shown that $K_La^*_w$ is related to $K_La^*_t$ by 1.85 power of surface tension.

In general, the effects of SAA on oxygen transfer are variable depending on the type of aeration method used. Additionally, the type of SAA used will no doubt influence the oxygen transfer rates.

For a more detailed study, some recommendations for future study can be pointed out.

1. Different types of SAA should be studied.
2. A wide range in concentration of SAA must be used.
3. Experimentation with wider range of power input and different scale.
4. Other types of aerators must be studied.
5. For scale up, experiments must be performed in different size vessels and in a full scale aeration tank.
6. Theoretical studies are required for a more fundamental understanding of the oxygen transfer precess.

REFERENCES

1. Metcalf and Eddy, Wastewater Engineering: Collection, Treatment and Disposal, McGraw-Hill, New York, 1972.

2. Baars, J.K. "The Effect of Detergents on Aeration: A Photographic Approach," J. of the Institute of Sewage Purification, 1955, pp.358-362.

3. Otoski, T., L.C. Brown, and R.G. Gilbert, "Bench and Full cale Studies for Alpha and Beta Coefficient Variability Determination," Paper presented at the 33rd Purdue Indusrial Waste Conference, Purdue Univ, Indiana, May9-11, 1978.

4. Downing, A.I., K.V. Melbourn, and A.M. Bruce, "The Effect of Contaminants on the Rate of Aeration of Water," J. Appl. Chem. Vol.7, No.11, pp.590-596,1957.

5. Downing, A.I. and G.A. Trusdale, "Some Factors Affecting the Rate of Solution of Oxygen in Water," J. Appl. Chem., Vol.5, No.10, pp.570-581, 1955.

6. Lewis, W.K. and W.G. Whitman, "Principles of Gas Absorption," Ind. Eng. Chem., Vol.16, No.12, pp.1215-1220, 1924.

7. Higbie, R., "The Rate of Absorption of a Pure Gas into a Still Liquid During Short Periods of Exposure," AIChE Trans., Vol.31, pp.365-388, 1935.

8. Danckwerts, P.V., "Significance of Liquid-Film Coefficient in Gas Absorption," Ind. Eng. Chem., Vol.43, No.6, pp.1460-1467, 1951.

9. Dobbin, W.E., "The Nature of Oxygen Transfer Coefficient in Aeration System," Biological Treatment of Sewage and Industrial Wastes, Reinhold Publishing Co., N.Y., 1955, pp.141,

10. Barnhart, E.L., "Transfer of Oxygen in Aqueous Solutions," J. Sanitary Engineering Divsion, ASCE, Vol.95, No.SA3, pp. 645-661, 1969.

11. Schwartz, A.T. and J.W. Perry, Surface Active Agents Vol.2, Interscience Publishers Inc., N.Y., 1958.

12. Gowdy, W.R., "Chemical Structure and Action of Synthetic Detergents," Sewage and Industrial Wastes, Vol.25, No.1, pp.15-19, 1953.

13. McKeown. J.J. and D.A. Okun, "Effects of Surface Active Agents on Oxygen Bubble Characteristics," J. Air and Water Pollution, Vol.5, No.2, pp.113-122, 1953.

14. Gameson, A.L.H., G.A. Truesdale, and R.A. Varley, "Some Factors Affecting the Aeration of Flowing Water," The Warer and Sanitary Engineer, pp.52-59, 1956.

15. O'Connor, D.J., "Effects of Surface Active Agents on Reaeration," J. Air and Water Pollution, Vol5, No.2, pp.123-133, 1963.

16. Carver, C.E., "Oxygen Transfer from Falling Water Droplets," J. the Sanitary Engineering Division, ASCE, Vol. 95, No.SA2, pp.239-251, 1969.

17. Mancy, K.H. and W.E. Barlage, "Mechanism of Interference of Surface Active Agents in Aeration Systems," in Advances in Water Quality Improvement, Ed. by Gloyna, E.F. and W.W. Eckenderfelder, Univ. of Texas Press, pp. 262-286, 1968.

18. Mancy, K.H. and D.A. Okun, "Effects of Surface Active Agents on Bubble Aeration," J. Water Pollution Control Federation, Vol.32, No.4, pp.351-364, 1960.

19. Downing, A.L. and A.G. Boon, "Oxygen Transfer in the Activated Sludge Process," in Advances in Biological Waste Treatment, Ed. by W.W. Eckenfelder and B.J. McCabe Reinhold Publishing Inc. N.Y., pp.131, 1963.

20. Stukenberg, J.R., V.N. Wahbah and R.E. Mckinney, "Experience in Evaluation and Specifying Aeration Equipment," J. Water Pollution Control Federation, Vol.49, No.1, pp.66-82, 1978.

21. Holroyd, A. and H.B. Parker, "Investigation on the Dynamics of Aeration," J. the Institute of Sewage Purification, pp.280-297, 1952.

22. Bewtra, J.K., W.R. Nicholas, and L.B. Polkowski, "Effects of Temperature on Oxygen Transfer in Water," Water Research, Vol.4, No.1, pp.115-123, 1970.

23. Bass, S.J. and G. Shell, "Evaluation of Oxygen Transfer Coefficients of Complex Wastewaters," Proceedings of the 32nd Purdue Industrial Waste Conference, May 10-12, pp.953-967, 1977.

24. Schmit, F.L., P.M. Thayer, and D.T. Redmon, "Diffused Air in Deep Tank Aeration," Proceedings of the 30th

Purdue Industrial Waste Conference, pp.576-588, 1975.

25. Eckenfelder, W.W. and D.L. Ford, "New Concepts in Oxygen Transfer and Aeration," in Advances in Water Quality Improvement, Ed. by E.F. Gloyna and W.W. Eckenfelder, Univ. of Texas Press, pp.215-236, 1968.

26. Kessener, H.J.N.H. and F.J. Ribbius, "Practical Activated Sludge Research," J. the Institute of Sewage Purification, pp.50-60, 1935.

27. ASCE, "Solubility of Atmospheric Oxygen in Water," J. The Sanitary Engineering Division, ASCE, Vol.86, No. SA4, pp.41-53, 1960.

28. APHA, Standard Method for the Examination of Water and Wastewater, 14th Ed, APHA, pp.446-447, 1976.

29. Montgomery, H.A.C., N.C. Thom, and A. Cockburn, "Determination pf Dissolved Oxygen by the Winkler Method and the Solubility of Oxygen in Pure Water and Sea Water," J. Appl. Chem., Vol.14, No.7, pp.280-296, 1964.

30. M. K. Stenstrom, "Models for Oxygen Transfer: Their Theoretical Basis and Implications for Industrial Wastewater Treatment," Proceedings of the 33rd Purdue Industrial Waste Conference, 1978.

31. Gilbert, R.G. and S.J. Chen, "Testing for Oxygen Transfer Efficiency in a Full Scale Deep Tank," Proceedings of the 31st Purdue Industrial Waste Conference, 1976.

32. Mueller, J.A., "Oxygen Transfer and Aeration," Summer Institute Nptes, Environmental Engineering Department, Manhattan College, New York, 1976.

33. Boyle, W.C., P.M. Bertheoux, and J.C. Rooney, "Pitfalls in Parameter Estimation for Oxygen Transfer Data," J. the Environmental Engineering Division, ASCE, vol.100, No.EE2, pp.391-408, 1974.

34. Haberman, W.L. and R.K. Morton, "An Experimental Study of Bubbles Moving n Liquids," ASCE Trans., Vol.121, pp.227-250, 1956.

35. Price, K.S., R.A. Conway, and A.H. Cheely, "Surface Aerator Interactions," J. the Environmental Engineering Division, ASCE, Vol. 9, No.EE3, pp.283-300, 1973.

36. Danckwerts, P.V., Gas-Liquid Reactions, McGraw-Hill, N.Y., 1970.

37. Manganelli, R. "Detergents and Sewage Treatment," *Sewage Works,* Vol.24, No.9, pp.1057-1068, 1057.

Appendix A. Experimental Data for Surface Aeration

Run	Temperature		DSS	Rotor		Torque	Power	C_s	K_La	
	Water	Air	conc.	Dia.	RPM				T^oC	20^oC
	^oC	^oC	mg/l	in	RPM	in-lbs	$x10^3$HP	mg/l	hr^{-1}	hr^{-1}
7	27.5	27.5	0	2	2100	0.436	2.31	7.36	9.23	7.95
8	27.5	27.5	0	2	2300	0.524	3.04	7.32	12.09	10.43
9	27.5	27.5	0	3	1500	1.613	6.11	7.20	22.90	19.74
10	26.0	26.0	0	3.5	1500	2.053	7.78	7.28	28.83	25.16
12	26.5	26.5	0	3.5	1625	2.251	9.24	7.44	31.26	27.48
70	26.2	26.5	0	3	1650	1.107	4.61	7.19	17.25	15.26
22	27.0	28.5	1	2	2400	0.590	3.57	6.86	9.86	8.59
23	28.0	28.0	1	3.5	1500	2.119	8.03	7.14	30.39	25.96
24	28.0	28.0	1	3	1500	0.953	3.61	7.33	11.20	9.56
73	27.0	27.0	1	3	1650	1.107	4.61	7.24	15.21	13.24

(continue)

79	29.0	30.0	1	3.5	1500	1.954	7.40	6.66	28.01	23.44
76	26.0	26.5	3	2	2600	0.667	4.38	7.70	11.59	10.29
77	25.6	26.5	3	2	2400	0.568	3.44	7.52	9.69	8.67
78	25.2	27.0	3	3.5	1500	1.987	7.53	7.69	23.19	20.92
18	27.0	27.0	5	2	2400	0.579	3.51	6.88	9.11	7.93
19	26.0	27.0	5	2	2500	0.634	4.00	7.24	9.99	8.87
20	26.0	27.0	5	3.5	1500	1.712	6.48	7.64	23.58	20.94
93	28.8	32.0	5	3.5	1400	1.723	6.09	6.76	18.44	15.49

Appendix B. Experimental Data for Diffused Aeration

Run	Temperature		DSS	Flow	Press.	Power	C_s	K_La	
	Water	Air	Conc.	Rate				T°C	20°C
	°C	°C	mg/l	SCFM	cm-Hg	$x10^3$HP	mg/l	hr^{-1}	hr^{-1}
13	26.0	30.0	0	0.419	5.26	4.60	7.94	6.25	5.55
27	26.5	24.0	0	0.363	5.00	3.72	6.98	6.12	5.38
33	26.5	23.0	0	0.313	4.76	3.06	7.22	5.89	5.18
34	26.0	23.5	0	0.363	4.76	3.55	7.34	5.95	5.28
28	26.0	25.0	1	0.412	5.16	4.37	7.00	6.13	5.44
64	27.5	28.0	1	0.363	5.16	3.88	7.22	6.08	5.24
74	26.8	26.5	1	0.363	5.04	3.78	7.29	6.03	5.27
94	32.5	30.0	3	0.412	5.04	4.34	7.07	5.61	4.38
95	32.0	30.5	3	0.363	5.04	3.83	6.88	5.95	4.69
96	32.0	32.0	3	0.314	4.88	3.23	6.79	5.96	4.70

(continue)

40	26.2	25.5	5	0.363	5.20	3.88	7.47	5.10	4.57
65	27.5	27.0	5	0.412	5.16	4.40	7.38	4.29	3.70
66	27.3	27.0	5	0.313	4.84	3.15	7.37	4.15	3.60
90	29.0	32.0	5	0.363	5.16	3.94	6.76	5.56	4.66
91	29.0	32.0	5	0.363	5.20	4.50	6.70	6.22	5.21
92	28.8	32.0	5	0.412	5.00	3.30	7.14	5.50	4.62
67	27.0	27.0	15	0.412	5.16	4.40	7.35	3.42	2.98
68	27.0	27.5	15	0.363	5.04	3.76	7.32	3.55	3.09
69	26.8	27.5	15	0.313	4.84	3.16	7.40	3.53	3.08

Appendix C. Experimental Data for Turbine Aeration

Run	Temperature		DSS	Compressed Air		Rotor	
	Water	Air	Conc.	Flow Rate	Press.	RPM	Torque
	°C	°C	mg/l	SCFM	in-Hg	RPM	in-lbs
14	26.0	30.0	0	0.345	1.77	700	0.491
46	26.0	25.0	0	0.240	1.97	690	0.579
47	26.0	26.0	0	0.304	1.97	760	0.678
48	26.0	26.0	0	0.387	1.97	840	0.755
49	26.8	26.5	1	0.245	2.00	690	0.579
50	26.5	26.5	1	0.313	2.00	770	0.667
51	26.5	26.5	1	0.372	2.00	820	0.777
82	26.0	28.0	1	0.343	1.77	810	0.634
84	29.0	31.0	3	0.262	1.77	750	0.535
85	29.0	31.0	3	0.343	1.77	820	0.634
86	29.0	31.0	3	0.381	1.77	875	0.722
87	28.8	30.0	5	0.269	1.77	750	0.534
88	29.0	32.0	5	0.343	1.77	820	0.634
89	29.0	32.5	5	0.417	1.77	875	0.722
52	26.0	24.0	15	0.235	2.00	700	0.568
53	26.2	27.5	15	0.313	2.00	770	0.667

(continue)

Run	Comp. Power	Rotor Power	$\frac{HP_c}{HP_r}$	Total Power	C_s	K_La	
						T°C	20°C
	$x10^3$HP	$x10^3$HP		$x10^3$HP	mg/l	hr^{-1}	hr^{-1}
14	1.33	0.87	1.53	2.20	7.32	8.35	7.42
46	1.00	1.01	1.00	2.01	7.25	10.43	9.26
47	1.28	1.30	0.98	2.58	7.29	10.88	9.75
48	1.63	1.60	1.03	3.23	7.17	11.52	10.23
49	1.05	1.01	1.04	2.06	6.93	9.58	8.42
50	1.35	1.30	1.04	2.65	6.93	10.11	8.89
51	1.60	1.61	0.99	3.21	7.14	11.21	9.85
52	1.31	1.30	1.01	2.61	7.04	10.61	8.88
84	1.01	1.01	1.00	2.02	6.79	8.07	6.75
85	1.32	1.31	1.01	2.63	6.75	10.36	8.67
86	1.61	1.61	1.01	3.20	6.78	12.44	10.41
87	1.03	1.01	1.02	2.05	7.04	7.93	6.64
88	1.33	1.30	1.02	2.65	7.00	10.40	8.70
89	1.62	1.60	1.01	3.21	7.10	11.80	9.87
52	1.00	1.00	1.00	2.00	7.36	8.88	7.88
53	1.35	1.30	1.04	2.64	7.68	10.09	8.93

NOMENCLATURE

a, b, A_w, B_w	constants
A	area normal to mass transfer
C	dissolved oxygen concentration (mg/l)
C_i	initial dissolved oxygen concentration
C_L	dissolved oxygen concentration in liquid
C_S	saturation dissolved oxygen concentration
C_S^*	apparent saturation dissolved oxygen concentration
d	bubble diameter
D_L	diffusivity (cm^2/sec)
e	efficiency
f	amount of oxygen absorbed during time of exposure per unit area
F	volumetric flow rate of air
HP_c	compressor power consumption (HP)
HP_r	impeller power consumption (HP)
K_L	liquid film coefficient
K_La	volumetric transport coefficient (1/min)
K_La^*	apparent volumetric transport coefficient
L	torque (in-lbs)
m	mass transfer
p	pressure (cm-Hg)
r	average frequency
R	gas constant
R_o	oxygen transfer rate per unit time and unit area

Re	Reynolds number
t	time
T	temperature
v	bubble rising velocity
V	volume of water in aeration tank
α	transfer coefficient correction factor for water contents
θ	transfer coefficient correction factor for temperature
μ	dynamic viscosity
ρ	water density
σ	surface tension
τ	probe time constant
ω	impeller rotational velocity