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Manuscript received February 18, 1960; revision received October 24, 1960; paper accepted October 26, 1960.

The Effect of Organic Substances on the Transfer of Oxygen from Air Bubbles in Water

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The liquid film coefficient is related to bubble diameter and velocity in pure water and to the physical properties of the liquid. The addition to water of organic substances which influence the surface tension and viscosity will decrease the size of the air bubble released from a diffuser and reduce the transfer of oxygen into the solution. The maximum reduction in oxygen transfer occurs in the region of maximum surface tension change. The effect of the addition of several organic substances on the oxygen transfer characteristics are shown.

Aeration involves the transfer of oxygen from air to a turbulent liquid. In diffused aeration air bubbles are formed at an orifice from which they break off and rise through the liquid, finally bursting at the liquid surface. The transfer process is considered to occur in three phases: during bubble formation, during bubble rise through the liquid depth, and as the bubble bursts at the liquid surface. Oxygen transfer during the initial and final phases of the bubble's life may be considered as end effects which will be substantially constant for a given aeration system.

In diffused aeration oxygen transfer during the bubble rise can be related to the characteristics of the bubbles released from a submerged orifice. The bubble characteristics can usually be defined in terms of a Reynolds number (*1*). At Reynolds numbers less than 300 to 400 the bubbles are spherical and act as rigid spheres. This corresponds to an approximate bubble diameter of 0.2 cm. Over a Reynolds number range of 400 to 4,000 the bubbles assume an ellipsoidal shape. In this range McKeown and Okun (*2*) have shown that the bubble formed has an inverted pear shape. In the early stages of the bubble's life, as it rises through the liquid, the bubbles are not in equilibrium with the surrounding liquid, and they oscillate between a fluid sphere and an elongated ellipsoid in decreasing amplitude. At Reynolds numbers greater than 4,000 the bubbles form spherical caps.

In the range of Reynolds numbers less than approximately 1,000 the liquid film coefficient in pure water has been related to the physical characteristics of the aeration system through an empirical correlation of the Reynolds and Sherwood numbers (*3*.) The end effects, which result in a decreasing transfer coefficent with increasing liquid depth, are included in the correlation as an exponential function of depth:

$$\frac{K_L D_B}{D_V} \cdot h^{1/3} = c \, \frac{D_B v_B \rho}{\mu} \qquad (1)$$

It was found that this empirical depth correction holds well for liquid depths in excess of 100 cm. Results obtained by several investigators and by the authors are shown in Figure 1. The effect of depth can also be estimated by plotting N_{Re}/N_{Sh} vs. liquid submergence depth. The average results and the spread of the data over a wide range of air flows and bubble diameters are shown in Figure 2. It is interpreted from this plot that extension of the curve to the ordinate (zero depth) estimates the end effects. Evaluation of the individual set of data employed in Figure 2 has shown that the slope and intercept of this form of plot vary somewhat with the bubble characteristics and the diffusion device. Further study is in progress to more theoretically define end effects during bubble aeration.

For the range of submergence depths normally encountered in aeration practice Equation (1) can be rearranged to define K_L for a specified operating condition:

$$K_L = c_1 \frac{v_B}{h^{1/3}} \qquad (2)$$

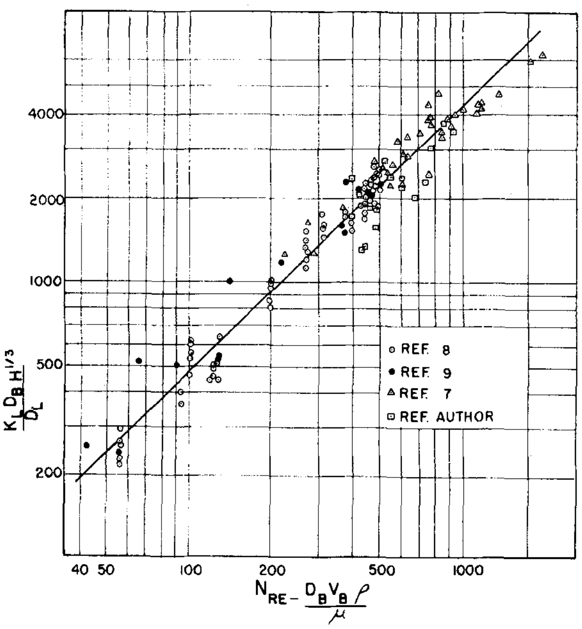

Fig. 1. Correlation of variables for oxygen transfer from air bubbles in water.

The relationship shown in Equations (1) and (2) covered a range of bubble diameter of 0.05 to 0.2 cm. and a range of depth of 3.0 to 12 ft.

When one considers bubble aeration systems in commercial aeration practice it is usually convenient to employ an over-all mass transfer coefficient K_La which can be defined by the following relationships.

The over-all oxygen transfer process can be defined as

$$N = K_L A \, (c_s - c_L) \qquad (3)$$

Equation (3) can be converted to concentration units

$$N/V = dc/dt = K_L \, A/V \, (c_s - c_L) \qquad (4)$$

and

$$K_La = K_L \, A/V \qquad (5)$$

For the case of bubbles rising through a liquid depth

$$A/V = \frac{6 \; G_s h}{d_B v_B V} \qquad (6)$$

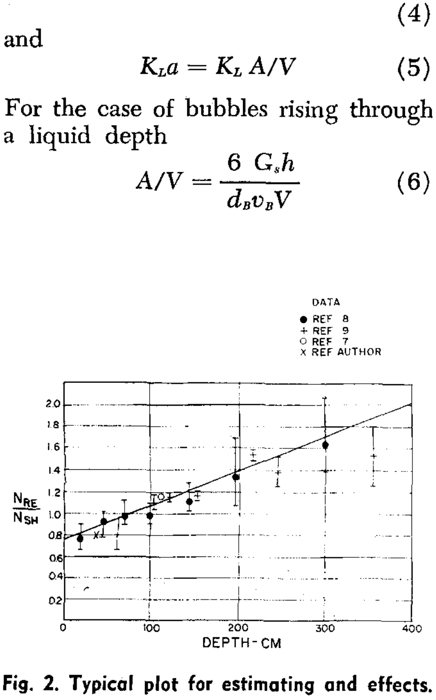

Fig. 2. Typical plot for estimating and effects.

Combining Equations (2), (5), and (6) one gets

$$K_La = \frac{c' \, h^{2/3} \, G_s}{V D_B} \qquad (7)$$

Since the interfacial area-volume ratio A/V cannot be measured in commercial aeration practice, it is convenient to employ the over-all transfer coefficient K_La to define the aeration process. Equation (7) has been employed to correlate the performance of several commercial air-diffusion devices (4). The correlation of data of several investigators has resulted in a value of n approximately equal to 2/3.

The oxygen transfer rate predicted by Equations (2) and (7) for pure water will vary markedly in the presence of small concentrations of surface active agents. The magnitude of the change in oxygen transfer rate depends on the concentration of contaminant and to a large extent on the nature of aeration and the characteristics of the aeration surface. The change in transfer rate becomes less pronounced as the surface agitation becomes more violent. Holroyd (5) has shown that in the presence of surface active agents the most significant reduction in K_L occurs at the bubble surface. A less severe depression of K_L was observed at a stagnant film surface and the least depression at a heaving water surface. At the heaving water surface it can be postulated that the short life of any interface restricts the formation of an adsorbed interfacial film.

EXPERIMENTAL APPARATUS AND PROCEDURE

An aeration column 5 cm. in diameter with a total liquid depth of 110 cm. was employed in these investigations. The column was jacketed by a second column 9 cm. in diameter to provide a circulating water bath for temperature control. Air was diffused through a nylon spinnerette ¾-in. in diameter with 20 holes each 35μ in diameter distributed over the surface. This device produced bubbles ranging from 0.12 to 0.16 cm. in diameter in pure water. The air flow was metered through a rotometer. Samples for dissolved oxygen measurement were withdrawn from a tap located 80 cm. from the base of the column. The experimental apparatus is shown in Figure 3. A series of oxygen transfer studies were also conducted employing an aloxite diffusor stone. The bubbles generated from this diffusor ranged in size from 0.03 to 0.06 cm. in diameter.

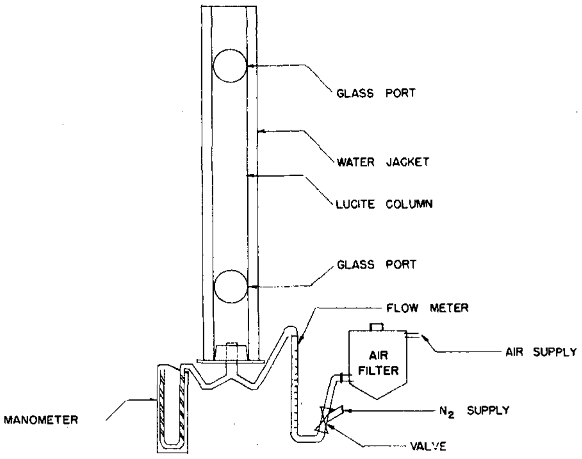

Fig. 3. Experimental aeration assembly.

Dissolved oxygen was measured with a manual polarograph with a dropping mercury electrode. The operating voltage for each substance studied was determined from a current-voltage curve. In each case the first oxygen plateau was used. Potassium chloride was added to each sample as a supporting electrolyte. For each series of test runs the polarograph was calibrated against the Winkler dissolved oxygen.

In order to define the bubble characteristics glass ports were placed in the column at 15 and 95 cm. above the spinnerette. The velocity and diameter of the bubbles were measured by photographing with a 35-mm. Reflex camera. A speed of 1/500 sec. was used to determine bubble diameter. A speed of 1/50 sec. was used to obtain streaks from which the bubble velocity

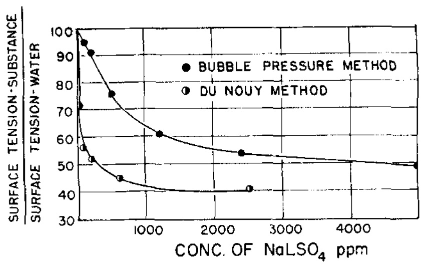

Fig. 4. Surface tension of sodium lauryl sulfate.

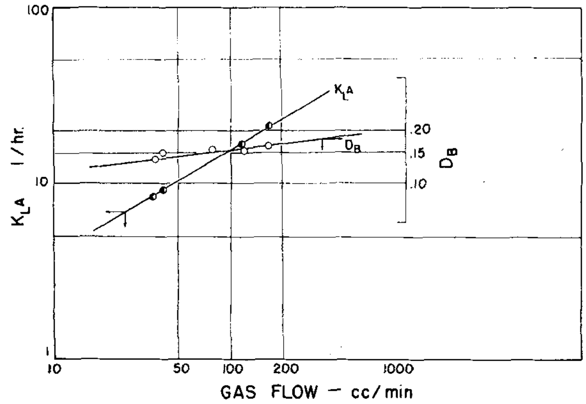

Fig. 5. Relationship between K_La, bubble diameter, and air flow for the 0.035-mm. spinerette.

was determined. The photos were developed as strip film and mounted as slides, and the average bubble characteristics were measured by projection on a screen.

Surface tension for the various substances and concentrations was determined by two methods. The equilibrium surface tension was determined by the platinum ring method with a tensiometer. The dynamic surface tension was determined by the method of maximum bubble pressure (6). Figure 4 shows a comparison of the results of the two methods for various concentrations of sodium lauryl sulfate.

The over-all transfer coefficient K_La was computed from the slope of a plot of the log of the saturation defect ($C_s - C_L$) vs. aeration time [Equation (4)]. The liquid film coefficient K_L was computed from Equations (5) and (6). In making these calculations it was assumed that the surface aeration at the top of the column was negligible, that the end effects were constant for any series of test runs, and that changes in oxygen saturation in the aeration column during a test run could be neglected.*

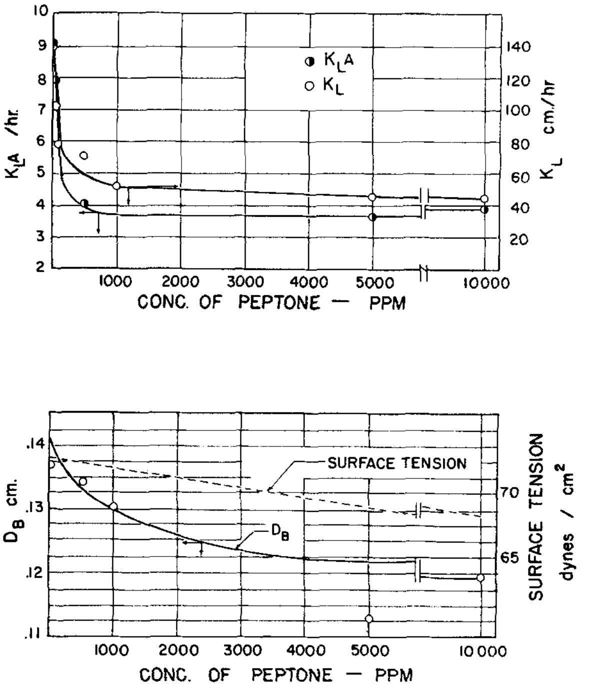

Fig. 7. Oxygen transfer characteristics in solutions of various concentrations of peptone.

Based on previous bubble aeration studies a temperature coefficient e of 1.02 was used to adjust all values to a temperature of 20°C.:

$$K_La\,(t°\text{C.}) = K_La\,(20°\text{C.}) \cdot 1.02^{(t-20)}$$

DISCUSSION OF RESULTS

The relationship between the over-all transfer coefficient, K_La and the gas flow G_s for the spinnerette used in this study is shown in Figure 5. For the range of gas flows employed the bubble size is dependent on the gas flow rate and the frequency of bubble formation is substantially constant:

$$d_B \sim G_s^{\,n} \tag{8}$$

By combining Equations (7) and (8) one can be shown that

$$K_La \sim G_s^{\,(1-n)} \tag{9}$$

The exponent $(1-n)$ for the spinnerette was found to be 0.15. The exponent for the Aloxite diffusor stone varied from 0.63 to 0.95 for various operating conditions.

The variation in K_La, K_L, d_B and σ with concentration for sodium lauryl sulfate, peptone, and heptanoic acid are shown in Figures 6, 7, and 8. For each of the three substances evaluated the liquid film coefficient initially decreased rapidly with increasing substrate concentration, followed by a slight increase at higher concentrations. All the values shown in this figure have been corrected to 20 deg. by the method previously described. With increasing concentration the mean bubble diameter and the surface tension decreased. The net effect on the over-

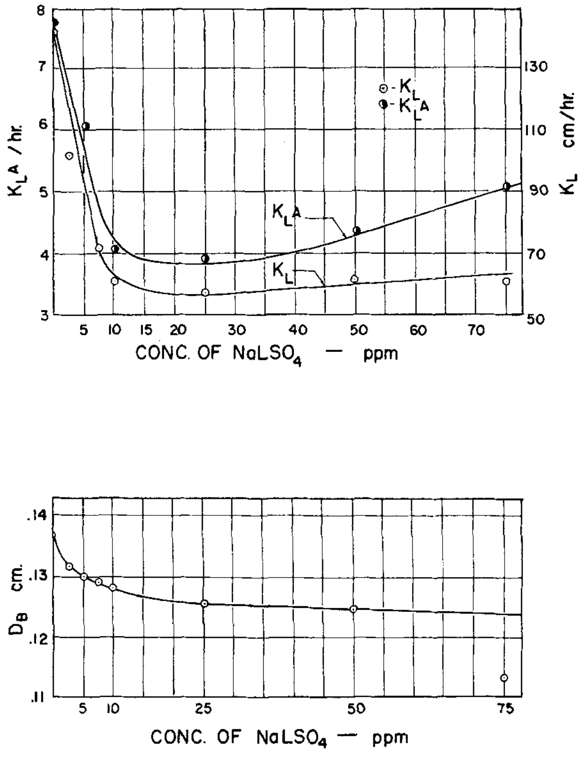

Fig. 6. Oxygen transfer characteristics in solutions of various concentrations of sodium lauryl sulfate.

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* Tabular material has been deposited as document 6883 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D.C., and may be obtained for $1.25 for photoprints or for 35-mm. microfilm.

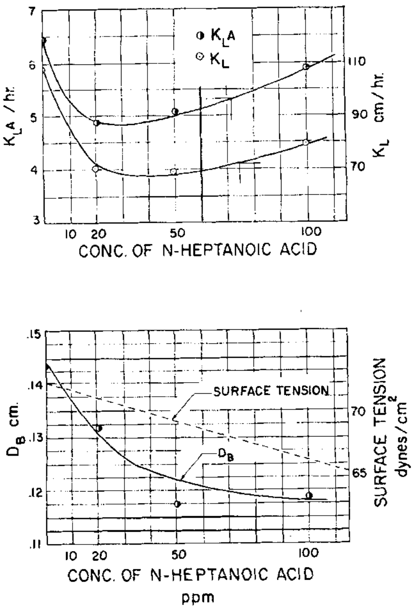

Fig. 8. Oxygen transfer characteristics in solutions of various concentrations of heptanoic acid.

all coefficient K_La was an initial decrease followed by an increase at higher concentrations.

A more dramatic picture of the changes of K_La with concentration of peptone is shown in Figure 9. These data were obtained with the Aloxite diffuser stone. The mean bubble diameter decreased from 0.048 cm. in water to 0.0235 cm. in a solution of 5,000 p.p.m. peptone. The liquid film coefficient initially decreased and then remained substantially constant at high concentrations. The large increase in K_La at high concentrations is primarily due to the large increase in the interfacial area-volume ratio A/V.

In bubble aeration the presence of surface active agents influence both the liquid film coefficient and the interfacial area-volume ratio A/V. In the case of each of the substances investigated in this study the liquid film coefficient initially decreased rapidly at low concentrations of surface active agent followed by a slight increase at higher concentrations. The sharp decrease in K_L occurred in the range of maximum surface tension change. The mean bubble diameter decreased with increasing concentration of each substance.

Similar results were reported by McKeown and Okun (*2*). They showed a maximum decrease in the liquid film coefficient of 67 and 53% for 8 and 4 to 10 p.p.m. of alkyl benzene sulfonate and Triton x-100 respectively. Their data also showed a slight recovery of K_L at higher concentrations of surfactant. It was indicated that this maximum depression of K_L occurred in the range of the critical micelle concentration.

It had been observed by other investigators that the nature of the aeration surface influenced the magnitude of change in K_L. O'Connor (*10*) determined the change in K_L in various concentrations of heptanoic acid in a system in which an unbroken liquid surface was mixed with a high-speed agitator. The ratio of K_L in various concentrations of heptanoic acid to the value in water for the two systems is shown below:

Concentration mg/l	Bubble aeration	Surface aeration
0	1.0	1.0
20	0.75	0.97
50	0.80	0.92
100	0.89	0.86

Scriven and Pigford (*11*) conclude from their work that surface active contaminants accumulate on the surface of the liquid film and there form a rigid or semirigid surface structure which drastically impedes liquid flow close to the surface. A highly compressed film of surface active material may itself offer appreciable resistance to the passage of solute molecules.

CONCLUSIONS

1. In bubble aeration in the presence of surface active agents the liquid film coefficient will initially decrease rapidly at low concentration, followed by a constant value or a slight increase at higher concentrations of surfactant. The maximum decrease in K_L will occur over the range of maximum surface tension change.
2. The mean diameter of bubbles produced by both the spinnerette and the Aloxite diffusor decreased with increasing concentration of surface active agent.
3. The over-all transfer coefficient initially decreased at low concentrations of surface active agent followed by an increase at higher concentrations. The increase is related both to the increase in K_L and to the increase in A/V.

ACKNOWLEDGMENT

This study was supported by Research Grant RG-4694, National Institute of Health, U. S. Public Health Service.

NOTATION

A = interfacial area for transfer
a = ratio of interfacial area to liquid volume
c, c', c'' = constants
c_L = dissolved oxygen concentration in the liquid
c_s = saturation of oxygen in water or waste at the mean depth and average oxygen concentration in the gas phase
D_v = diffusivity of oxygen in water
D_B = mean diameter of air bubble
G_s = air flow
h = tank liquid depth
K_L = over-all liquid film coefficient, (cm./hr.)
K_La = over-all oxygen transfer coefficient, (1/hr.)
n = gas rate exponent
N = total oxygen transfer
N_{Re} = Reynolds number $d_B v_B \rho / \mu$
V = volume of liquid under aeration
v_B = volume of air bubble relative to tank liquid
σ = surface tension
N_{Sh} = $K_L D_B / D_v$

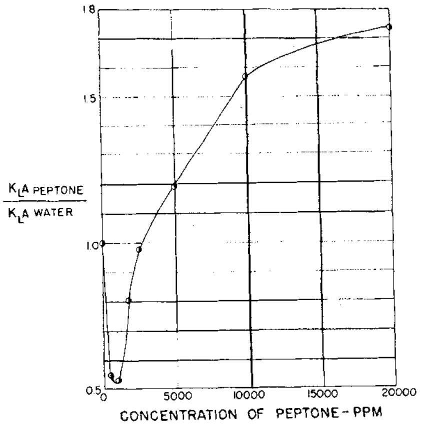

Fig. 9. Variations in K_La with concentrations of peptone.

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Manuscript received January 18, 1960; revision received April 12, 1961; papers accepted April 19, 1961. Paper presented at A.I.Ch.E. Atlanta meeting.