Bubble Aeration of Water in the Presence of Some Organic Compounds

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THE SIZE of air bubbles as well as the rate of oxygen transfer from the bubbles to water may be affected by the presence of small quantities of some organic substances (*2, 3, 4*).

The authors (*5*) found that the rate of oxygen transfer from air bubbles to water is increased when small quantities of some alcohols, esters, or carboxylic acids are added to the liquid phase. 4-Methyl-2-pentanol proved to be one of the more effective in this respect. At a concentration of 6.6 p.p.m. it increased the rate of oxygen absorption by 100%.

This effect is of interest in aeration practice, since the economy of this operation depends to a great extent on the rate of oxygen absorption.

Objectives of this work were to conduct a more comprehensive study of the effects of higher alcohols, esters, and carboxylic acids on the rate of oxygen transfer from air bubbles to water and to find out to what extent this effect depends on the way the substance is introduced into the aerated water. Preliminary tests showed that when the substance is introduced continuously at the surface of the aerator located in a stream of water, the small bubbles formed maintain their size, even though its concentration in the bulk of water is negligible.

It seemed possible, therefore, that in this way a smaller amount of the substance would be required to produce the same effect as in a solution of a uniform concentration.

EXPERIMENTAL PROCEDURE

A schematic diagram of the test equipment is shown in Figure 1. The solid lines represent the parts used in batch aeration tests for evaluation of the relative effects of the investigated substances on the rate of absorption. The dashed lines indicate the additional equipment and instruments used in continuous (steady-state) tests, in which the substance was continuously introduced at the surface of the aerator.

The absorption column was made of borosilicate glass, 36 inches high, with an inside diameter of 8 inches. The air was introduced through an Aloxite plate (Grade 1) of 1-inch diameter.

In all batch aeration tests the column was filled with 25 liters of distilled water and the temperature adjusted to 25° C. The height of the water column above the plane of the aerator was 28 inches and was kept constant in all tests of this group. The water was deoxygenated by means of nitrogen. At the end of the deoxygenation period a known quantity of the investigated substance was dissolved in water and the flow of nitrogen was continued for another few minutes to ensure uniform concentration.

The rate of flow of air was 770 cc. per minute (STP) in all tests discussed. At constant time intervals samples of the solution were withdrawn through the sample line and analyzed for dissolved oxygen content by the Winkler method (*1*).

All substances investigated were checked for possible interference with the Winkler method. No interference was observed within the range of concentrations used.

In the batch tests the rate of absorption was calculated by the equation:

$$\frac{dc}{dt} = \frac{10^6}{W} K_L A \, (C_i - C_1) \qquad (1)$$

in which

C = dissolved oxygen concentration, p.p.m.
t = aeration time, hours
W = weight of water, grams
K_L = oxygen transfer coefficient, based on liquid film resistance, grams of oxygen per hour per sq. cm. per unit concentration difference, p.p.m.
A = instantaneous contact area of bubbles, sq. cm.
C_i = equilibrium concentration of oxygen, p.p.m.
C_1 = concentration of oxygen in water at any time, p.p.m.

Assuming C_1 and A as independent of time (*3, 7*), integration of the equation gives:

$$K_L A = \frac{2.3\,W}{10^6} \left[\frac{\log (C_i - C_0)/(C_i - C_1)}{t} \right] \qquad (2)$$

where C_0 is the initial dissolved oxygen concentration at time t_0. The C_i values are the average equilibrium concentrations. The values of C_1 from the absorption curve were used to plot the logarithmic term against time. The numerical value of the slope of the resulting straight line was then used to calculate $K_L A$.

The effect of an investigated substance on the rate of oxygen absorption was expressed in terms of the ratio $[K_L A]_R / [K_L A]_W$, where subscripts R and W refer to the solution and distilled water, respectively. It is a measure of the combined net effect resulting from the changes in

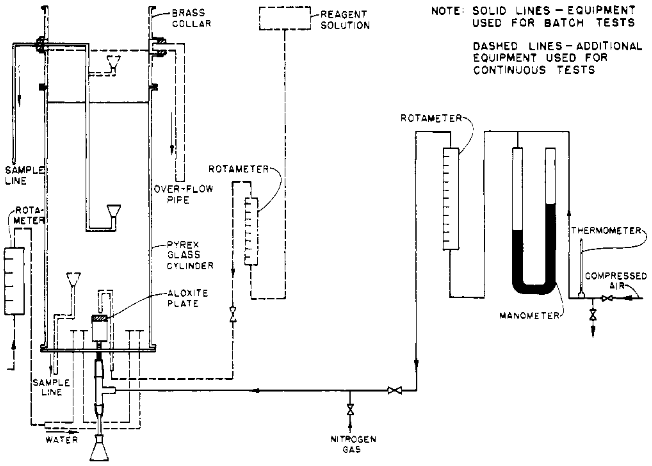

Figure 1. Schematic diagram of experimental equipment

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the surface area of absorption and in the mass transfer coefficient. Both $[K_LA]_R$ and $[K_LA]_W$ were determined under the same experimental conditions. From a number of tests $[K_LA]_W$ was found to be 0.148, and this value was used as a reference base in all the batch tests. The probable error attached to this value was ±0.001 and the probable error of each determination was ±0.0023. During the course of the work tests were conducted to check for possible change in the reference base. However, the differences in results were too small to warrant a correction.

In the continuous (steady-state) aeration tests deoxygenated distilled water was introduced at the bottom of the column and removed at the top through an overflow pipe (see Figure 1). The rate of flow of water was 7570 cc. per minute and the flow of air 770 cc. per minute (STP) in all tests of this group.

When the flows of air and water had been adjusted to the above values, a solution of 4-methyl-2-pentanol of a known concentration was introduced into the column through a glass tube located directly above the Aloxite plate.

The tests were conducted at three different rates of flow of the alcohol solution. At each flow rate the concentration of the solution was adjusted to maintain a constant concentration of 1 p.p.m. in the bulk of the aerated liquid.

During the tests samples were withdrawn from two sampling points located 3 inches above the Aloxite plate and 2 inches below the surface of the solution and were immediately analyzed for D.O. content. The D.O. concentration of the water entering the column was checked at constant time intervals. As in the batch tests, distilled water was used as a reference.

The tests with water were conducted under the same test conditions, except that instead of the alcohol solution distilled water was introduced at the plate at the same rates of flow as in the alcohol tests, to compensate for (in evaluation of the results) the effect of shear produced by the stream of water (or solution) flowing against the surface of the plate.

The results of the tests were calculated from the oxygen balance and the average oxygen concentration gradient at the planes of the two sampling points, under steady-state conditions.

As expressed in previous tests the results are known as $[K_LA]_R/[K_LA]_W$ ratios.

DISCUSSION OF RESULTS

Effect of Higher Alcohols on Rate of Oxygen Absorption. The effects of isoamyl alcohol, 4-methyl-2-pentanol, *n*-heptyl alcohol, 2-ethyl-1-hexanol, and *n*-octyl alcohol were evaluated in the batch absorption tests.

Even at the low concentration used (1 to 30 p.p.m.), all of these alcohols decreased the size of the air bubbles considerably. Their effect on the rate of absorption is shown in Figure 2.

In the case of isoamyl alcohol, 4-methyl-2-pentanol, and *n*-heptyl alcohol on increasing the concentration a maximum is reached. However, the values of this maximum effect decrease with increasing molecular weight of these alcohols. In the previous investigation (*5*) this change in the maximum effect was less pronounced in the case of lower alcohols. The higher the molecular weight of the alcohol, the lower is the concentration at which the maximum occurs.

Under the operating conditions used in this work isoamyl alcohol, at a concentration of 18 p.p.m., increased the rate of absorption more than three times, while 4-methyl-2-pentanol increased absorption rate to only 2.5 times that in pure water.

However, in the region of lower concentrations 4-methyl-2-pentanol was more effective. Inspection of the corresponding curves shows that at a concentration of 5 p.p.m. 4-methyl-2-pentanol increased the rate two times, while isoamyl alcohol increased the rate only 1.5 times. A similar trend can be observed in the case of *n*-heptyl alcohol, which at concentrations below 2.5 p.p.m. appears more effective than the other two alcohols.

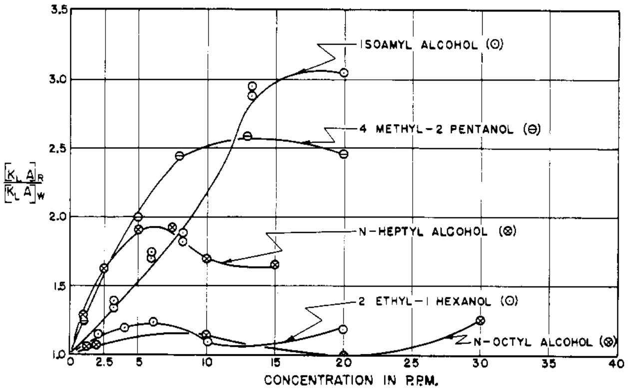

Figure 2. Effect of alcohols on rate of oxygen transfer

Both 2-ethyl-1-hexanol and *n*-octyl alcohol showed a much smaller effect and a different behavior. On increasing the concentration of the alcohols the rate of absorption at first increased, reaching a maximum which was followed by a minimum in the region of higher concentration.

The results of these tests indicate that the higher the alcohol molecular weight the smaller is its maximum effect on the rate of absorption. It is possible that this drop in effectiveness was the result of an increased resistance to oxygen transfer, which was more pronounced in case of higher alcohols.

The results discussed apply to the system and operating conditions used in the tests. A change in the aerator system or in the rate of flow of air may influence the effectiveness of a substance (*5*).

Effect of Some Esters on Rate of Oxygen Absorption. Figure 3 presents the results of tests conducted in dilute solutions of five esters. The effects of the esters were very similar to those of the alcohols. Except for ethyl acetate, which was not investigated at higher concentrations, increase in ester concentration was followed by a sharp increase in the rate until a maximum was reached. A further increase in concentration had only a small effect, except in the case of isoamyl acetate, where increase in concentration beyond the maximum point caused a sharp decline in the rate of absorption, followed by a gradual recovery.

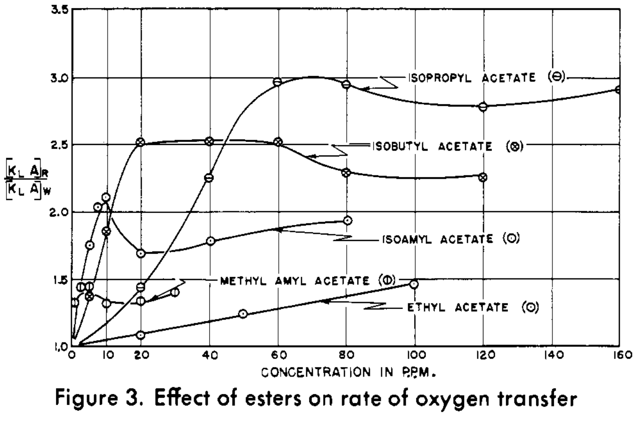

Figure 3. Effect of esters on rate of oxygen transfer

Again here, as in the case of higher alcohols, the values of the maxima decrease progressively with increasing molecular weight of the esters. The concentrations at which the maxima occur are consistently lower for esters of higher molecular weight.

Thus isopropyl acetate, which showed the most pronounced effect at concentrations between 60 and 80 p.p.m., is considerably less effective than isobutyl acetate at concentrations below 40 p.p.m. Isoamyl acetate is still more effective than the other two at concentrations below 10 p.p.m.

Methyl amyl acetate, which showed the lowest position of the maximum, appears to be more effective than the other esters at concentrations below 2 p.p.m.

Most of the curves (Figure 3) indicate the possibility of another maximum in the region of higher concentrations.

As in the case of alcohols, the esters showed a marked effect on the size of the air bubbles. Figure 4 compares the degree of dispersion of air in water with that in a solution containing 10 p.p.m. of isoamyl acetate. The pictures were taken under otherwise the same operating conditions, indicating the relative bubble sizes. In this case, the improvement in the rate of absorption was more than 100%.

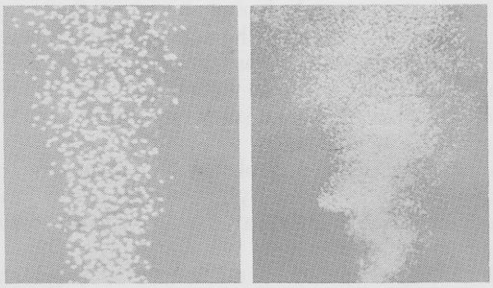

Figure 4. Effect of isoamyl acetate on bubble size

Left. Distilled water
Right. 10 p.p.m. isoamyl acetate solutions

Effect of Higher Carboxylic Acids and Tergitol 08 on Absorption Rate. The two carboxylic acids investigated in this group of tests were *n*-caproic and octanoic acids (Figure 5). *n*-Caproic acid is very effective in improving the rate of oxygen transfer, which at a concentration of 15 p.p.m. was about 2.7 times greater than in pure water. The octanoic acid showed a much lower maximum effect but proved more effective than the *n*-caproic acid at concentrations below 3 p.p.m. This is in agreement with the behavior of the alcohols and esters.

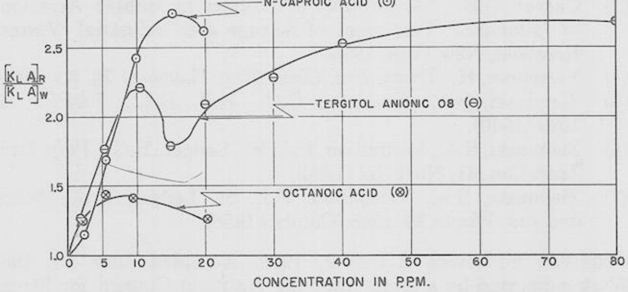

Figure 5. Effect of some acids and Tergitol 08 on rate of oxygen transfer

Figure 5 includes also the results of tests conducted with an anionic surface active agent (Tergitol 08). Contrary to the behavior of some previously investigated surface active agents (5), Tergitol 08 was very effective in a wide range of concentrations. It showed a characteristic drop in effectiveness beyond the maximum, followed by a gradual recovery, a behavior similar to that observed in case of some of the higher alcohols and esters.

CONTINUOUS FLOW TESTS

The tests so far conducted showed that some organic substances at very low concentrations (2 to 10 p.p.m.) exhibit a pronounced effect on the rate of oxygen absorption. Since some of the more effective substances are commercial products of comparatively low cost, the possibility of their application in aeration processes should be considered. In an attempt to improve the effectiveness of this procedure two ways of approach were further investigated. Both were based on the results of tests which indicated that the effect of the substance depends primarily on its concentration at the air-diffusing surface. Once the small bubbles are formed, they tend to maintain their size even when the concentration of the substance in the bulk of the aerated liquid is much smaller.

In the first approach the investigated substances were introduced in the form of vapor, together with the stream of air. A number of different alcohols and esters were used in these tests. Despite a wide range of concentrations applied, no change in the size of air bubbles was observed in any of these tests. Investigation in this direction was therefore discontinued.

In the second approach the investigated substances were introduced in the form of a solution through a tube terminating at the air-dispersing surface. The solution was, in this way, continuously introduced into the stream of water flowing through the aeration column, thus maintaining a higher concentration in the vicinity of the aerator.

This method of introduction proved to be very effective and was investigated at different operating conditions.

The concentration of a substance introduced at the air-diffusing surface depends on a number of factors, such as the concentration, the rate of flow of the introduced solution, and the rate of mixing, which in turn depends on the air flow and the geometry of the system.

The system used in this work consisted of an Aloxite plate and a glass tube located about 1/16 inch above the center of the plate.

A solution of 4-methyl-2-pentanol was introduced through the glass tube and allowed to flow over the surface of the plate. This system did not maintain a uniform concentration of alcohol over the surface of the plate. As a result of the random water flow pattern, some parts of the plate were not brought in contact with the inflowing solution.

This arrangement had, however, the advantage of a simple system and gave good reproducibility of results.

The concentration of the aerated solution, leaving the column, was 1 p.p.m. in all tests. The tests were conducted in duplicate at three different flow rates of the entering solution. The concentrations of these solutions were selected to produce the required alcohol concentration in the aerated liquid.

Despite the same final concentration, the effect of the alcohol solution depends on its rate of flow and concentration (Figure 6).

Under experimental conditions the maximum effect was obtained at a rate of flow of the alcohol solution of 150 cc. per minute and concentration of 50.3 p.p.m. The occurrence of such maximum appears to be logical. At lower rates of flow of the alcohol solutions of corresponding higher concentrations, the alcohol was not evenly distributed over the whole surface of the plate. At higher rates of flow of the alcohol solutions, of correspondingly lower concentrations, the uniformity of distribution was better but the concentration and therefore the effect of the alcohol were smaller.

This maximum corresponds to an increase in the rate of absorption by 50% over that in pure water under the same test conditions (Figure 6).

Reference to Figure 2 shows that twice as high an alcohol concentration was required to effect a 50% improvement in absorption rate in the case of aeration of a solution of a uniform concentration.

The results of these tests indicate that in continuous aeration systems, in which the substance is introduced at the air-dispersing surface, lower bulk concentration is required to produce the same effect as in aeration of a solution of a uniform concentration.

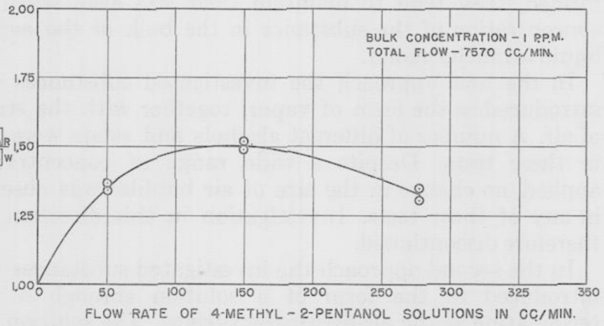

Figure 6. Effect of continuous introduction of 4-methyl-2-pentanol solutions at zone of bubble formation

Figure 7 illustrates the effect of sulfite waste liquor (S.W.L.) on the size of air bubbles, in a solution of a uniform concentration and in a stream of water to which the liquor was continuously introduced at the air-diffusing surface. In each case the bubbles were produced by the same porous plate and at the same rate of flow of air.

The middle picture shows the air bubbles formed in a S.W.L. solution of a uniform concentration of 120 p.p.m. (dry basis). The right-hand picture was taken at the same bulk concentration of the liquor, which, however, in this case was introduced at the plate by the method described above.

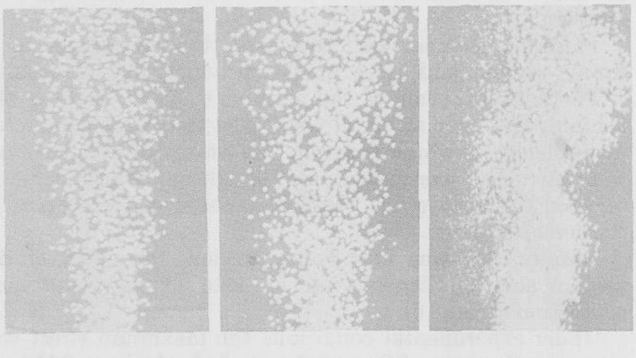

Figure 7. Effect of sulfite waste liquor on bubble size

Left. Distilled water (continuous system)
Center. 120 p.p.m. S.W.L. solutions (batch system)
Right. 120 p.p.m. S.W.L. solutions (continuous system)

While there is practically no change between the size of air bubbles formed in distilled water and in the solution of S.W.L. of uniform concentration, there is a marked decrease in their size when the S.W.L. is introduced at the porous plate.

The effectiveness of this method depends primarily on maintaining a high and uniform concentration of the substance at the air-diffusing surface.

The rotary aerator designed by one of the authors (*6*) appears to have some advantages in this respect. The solution of a given substance (or S.W.L.) could be introduced inside the aerator and dispersed with air through the perforations of the rotary cylinder. In this way a more uniform distribution of the solution could be obtained, and a more intimate mixing achieved, between the solution and the air leaving the aerator.

CONCLUSIONS

Tests conducted in dilute solutions of isoamyl alcohol, 4-methyl-2-pentanol, *n*-heptyl alcohol, 2-ethyl-1-hexanol, and *n*-octyl alcohol showed that, at the low concentrations used (1 to 30 p.p.m.), all of these alcohols decrease the size of the air bubbles considerably.

In the case of isoamyl alcohol, 4-methyl-2-pentanol, and *n*-heptyl alcohol increasing the concentration increases the rate of absorption until a maximum is reached. However, the value of this maximum effect and the concentration at which it occurs decrease with increasing molecular weight of the alcohol.

A similar behavior was observed in the case of esters (isopropyl, isobutyl, isoamyl, methyl amyl, and ethyl acetates) and two higher carboxylic acids (*n*-caproic and octanoic acids).

Both 2-ethyl-1-hexanol and *n*-octyl alcohol showed a much smaller effect and a different behavior than the lower alcohols. On increasing their concentration the rate of absorption at first increased, reaching a maximum which was followed by a minimum in the range of higher concentrations.

Tests conducted under continuous flow conditions indicate that the effect of a given substance on the rate of absorption depends primarily on its concentration at the air-diffusing surface.

Aeration tests performed in the presence of 4-methyl-2-pentanol showed that if the solution of this alcohol was introduced in the zone of bubble formation, a smaller alcohol concentration was required to produce the same effect as in aeration of a solution of a uniform concentration.

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