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Hydrodynamic Effect of Surfactants on Gas-Liquid Oxygen Transfer

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An experimental investigation of the hydrodynamics at the surface region of the liquid reveals that the soluble surfactants (sodium lauryl sulfate, glucose oxidase, and bovine serum albumin) affect both the length and the velocity scales of liquid eddies approaching the surface, which results in a decrease in mass transfer.

SCOPE

The effect of surfactant on gas-liquid mass transfer has been studied by numerous investigators due to its importance in industrial applications. For nonflow systems, surfactants were shown to exert considerable mass transfer resistances (Plevan and Quinn, 1966; Burnette and Himmelblau, 1970), whereas for flow systems such as falling films (Cullen and Davidson, 1956), stirred cells (Goodridge and Robb, 1965; Springer and Pigford, 1970), and channel flows (Moo-Young and Shoda, 1973), an additional effect, namely, the hydrodynamic effect was reported. This "hydrodynamic effect" means that the surfactant film at the surface of the liquid changes the interfacial hydrodynamics so that the mass transfer is reduced. Although it was shown theoretically (Davies, 1972) how the liquid eddy velocity is damped due to the surfactant, a detailed investigation of the "hydrodynamic effect" has been difficult mainly due to experimental limitations.

The objective of this study is to investigate the effect of some soluble surfactants on interfacial hydrodynamics for the oxygen absorption through a flat surface of a stirred cell. An oxygen ultra-microprobe was used for estimating the length and the velocity scales of liquid eddies approaching the surface.

CONCLUSIONS AND SIGNIFICANCE

The hydrodynamic effect was shown to be further broken down to two effects: an increase in the length scale and a decrease in the "equivalent" velocity scale of liquid eddies approaching the surface. The details of the hydrodynamic effect were different depending on the individual surfactant.

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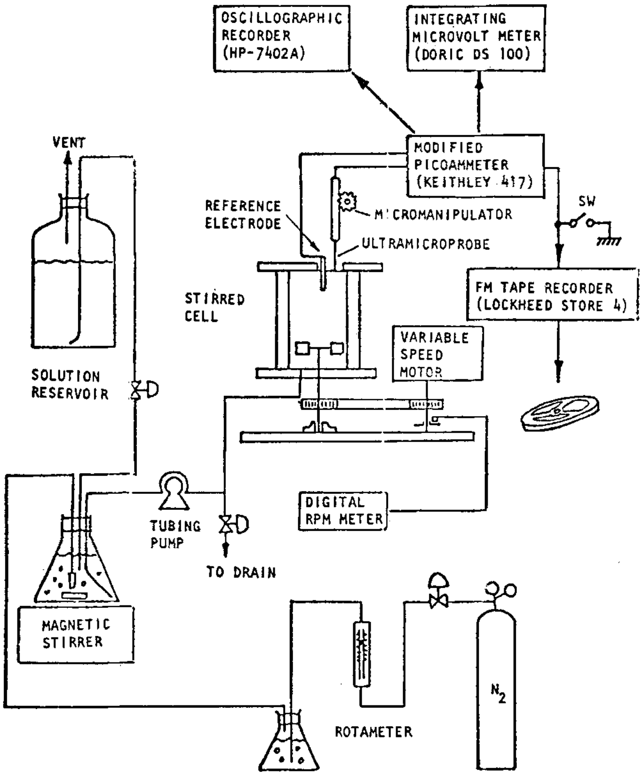

Figure 1. Overall experimental setup.

EXPERIMENTAL

The ultra-microprobe used in this study was essentially an extremely miniaturized polarographic oxygen sensor. The probe was of the same type used earlier (Bungay et al., 1973; Tsao and Lee, 1975), but was further refined (Lee et al., 1978) to have better spatial resolution and faster response time (90% response time of less than 50 msec). Briefly, the ultra-microprobe consists of a long glass-insulated needle with a membrane-covered sensing tip of less than 1 micron. It was shown (Lee et al., 1978) that the surfactants and other contaminants do not interfere with the measurement when the probe is properly designed. An Ag-AgCl electrode was used as the reference electrode.

The surface active agents used were bovine serum albumin (BSA), glucose oxidase (GO), and sodium lauryl sulfate (SLS), all of which were of the reagent grade. A Fischer Du Nuoy ring type tensiometer was used for the surface tension measurements.

A fully-baffled stirred cell, constructed from 73 mm I.D. plexiglass tubing, 90 mm long, was used as the absorption cell. The cell had four baffles of 6.5-mm width and was equipped with a six-bladed turbine impeller of 50-mm diameter. Figure 1 shows the details of the experimental setup.

Initially, the cell was thoroughly soaked and washed with distilled water to leach out most of the surface active materials present in the plexiglass. A satisfactory condition was confirmed when no change in measured surface tension was observed before and after each run. Since the polarographic sensor requires a small amount of electrolyte in the solution, 0.2% by weight NaCl was used as the base solution for making up solutions of the desired surfactant concentrations. The test solution was stripped of the dissolved oxygen by nitrogen-sparging before each run. The surface area for absorption was small (25 mm in diameter), so the change in bulk concentration of the dissolved oxygen was very small for each experimental run.

After the impeller speed was stabilized as indicated by a constant reading on a digital RPM meter, the probe was lowered by a micromanipulator (a high-precision micrometer) until the probe was placed at a predetermined depth from the liquid surface. The current output from the probe was first amplified with a picoammeter (Keithley Model 417 with modification to incorporate polarization voltage source) and then recorded on a FM recorder (Lockheed Model Store 4). The taped data was then digitized with a hybrid computer (EAI 680 and CDC 1700) and the final numerical analysis was performed by CDC 6500 digital computer. Details of the experimental procedures, the data acquisition methods, and the computer programs are available elsewhere (Lee, 1977).

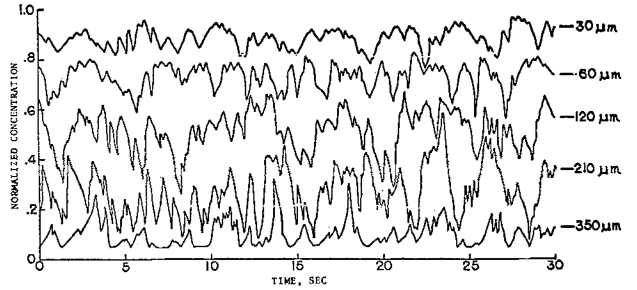

Figure 2. Concentration fluctuation recordings at different depths from the surface for a clean liquid at 60 RPM.

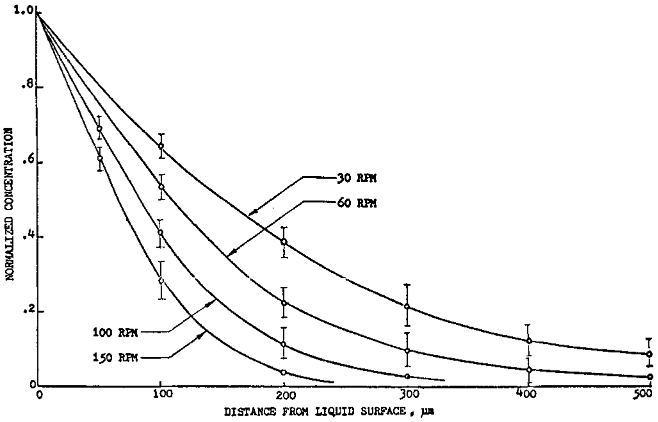

Figure 3. Normalized concentration profiles at the gas-liquid interface for a clean surface at different impeller speeds.

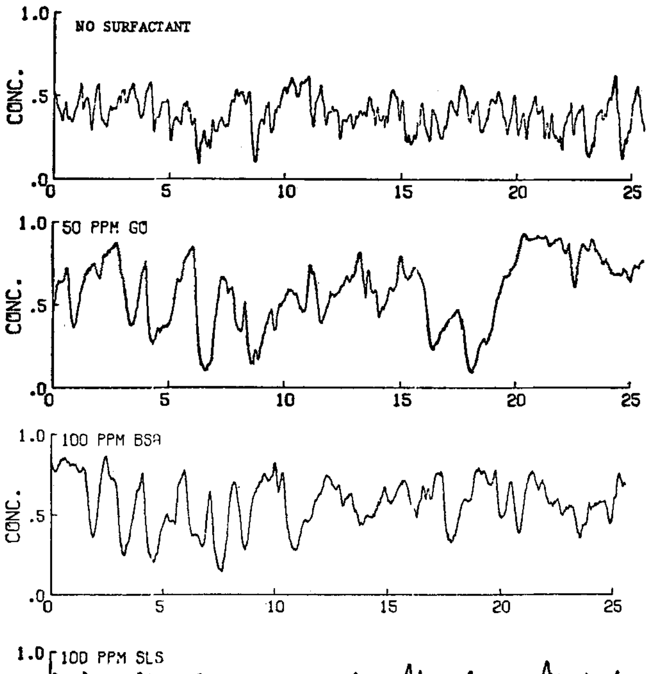

Figure 4. Concentration fluctuation recordings for different surfactant solutions at 100 μm below the liquid surface at 100 RPM.

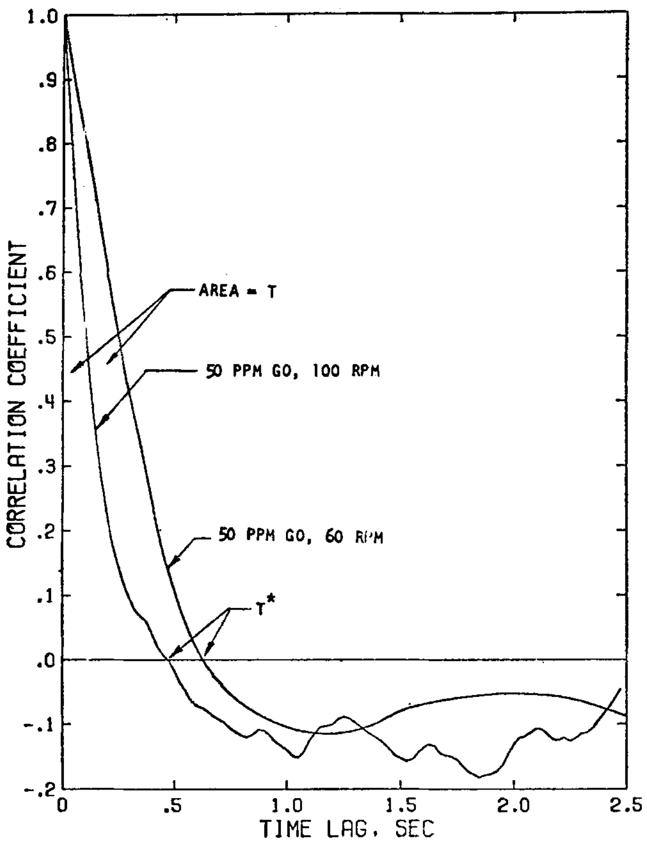

Figure 5. Auto-correlation coefficient curve for estimating the averaged period, *T*.

Extreme care was taken to avoid any vibration of the stirred cell during the measurement. Up to 30 μm of low frequency ripples were detected at 150 RPM with a clean surface, but the surface ripples were negligible when the surfactant was added. The position of the probe where all the measurements were made was at the midpoint between the center and the wall of the opening (Figure 1). The measurements were done at room temperature which was maintained at 23 ± 1°C.

The impeller Reynolds number covered in this study was 1250 to 6250, which corresponds to the transient region. The mass transfer coefficient, k_L, ranged from 0.4×10^{-3} to 1.72×10^{-3} cm/s. Higher impeller speeds could not be used due to excessive surface ripples.

DATA ANALYSIS

Figure 2 illustrates an example of concentration recordings at different depths (as indicated by the numbers on the right-hand side of Figure 2) from the surface of the liquid. By taking the mean values of concentration at different depths, concentration profiles were constructed. Figure 3 shows the concentration profiles for a clean water surface at different impeller speeds. The local mass transfer coefficients were then calculated from the measured concentration profiles:

$$(k_L)_{\text{local}} = \left[-D_o \left(\frac{\partial c}{\partial x} \right)_{x=0} / (c_i - c_b) \right]_{\text{local}} \tag{1}$$

where D_o, c_i, and c_b are oxygen diffusivity, surface concentration, and bulk concentration, respectively. The diffusivity of oxygen, D_o, for clean water was experimentally determined as 2.23×10^{-5} cm^2/s (Lee, 1977) which agrees well with the published data (St-Denis and Fell, 1971). Since the changes in oxygen diffusivity were very small (Lee, 1977) in the range of surfactant concentrations used, the diffusivity for the clean liquid was used throughout.

Some of the concentration fluctuation measurements are given in Figure 4. It is shown that, given the same impeller speed, the fluctuation frequency changes markedly upon adding the surfactants. In general, the high-frequency component is suppressed with the added surfactant, but the trend was different depending on the surfactant used. The method of obtaining hydrodynamic parameters from these data is given below.

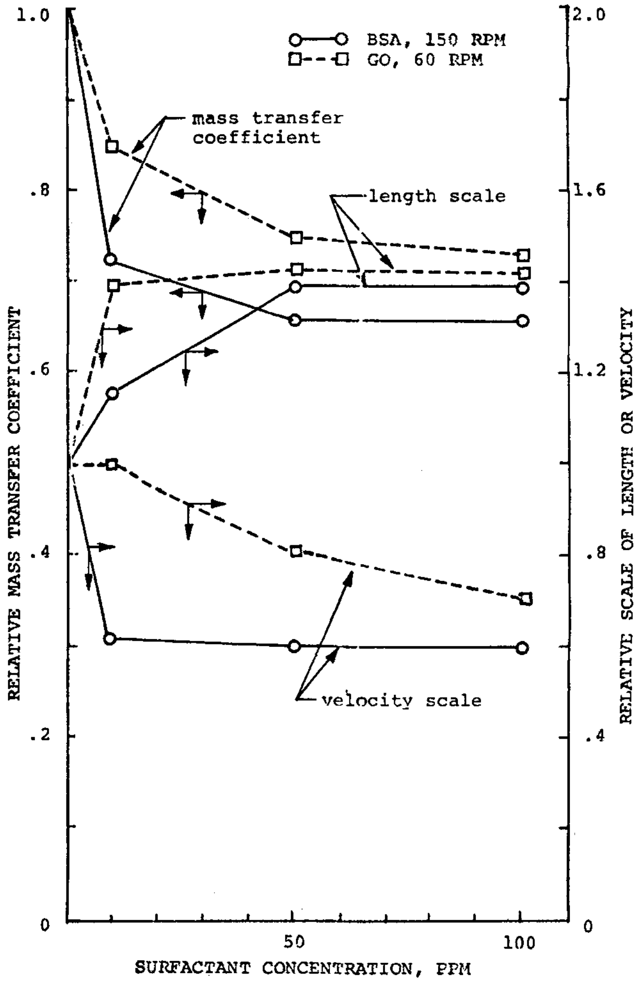

Figure 6. Relative values of k_L, *L*, and *V* vs. surfactant concentrations (*V* and *L*: 100 μm below surface).

The length scale, L, of eddies approaching the liquid surface was estimated from the auto-correlation of the fluctuating concentrations. The method was essentially the same as that used for obtaining Eulerian length scale of eddies (Hinze, 1959): if the liquid moves parallel to the surface with an average velocity of U, the length scale, L, becomes:

$$L = UT \tag{2}$$

where T is the statistically averaged period of fluctuation. It was shown (Hinze, 1959) that T is the area under a curve of auto-correlation coefficient, $R(\tau)$, plotted against the time lag, τ, where,

$$R(\tau) = \frac{[c(t)c(t+\tau)]_{\text{av}}}{[c^2(t)]_{\text{av}}} \tag{3}$$

The $R(\tau)$ was computed from the digitized data via the fast Fourier transform method described by Bendat and Piersol (1971). Figure 5 shows two examples of $R(\tau)$ as a function of τ. The T was taken as the area under the curve $R(\tau)$ from 0 to T^* (Figure 5).

If U is assumed to remain unchanged with the added surfactant, the change in L due to the surfactant can be estimated as:

$$\frac{L_s}{L_o} = \frac{UT_s}{UT_o} = \frac{T_s}{T_o} \tag{4}$$

where the subscripts s and o designate with and without surfactant, respectively. The above assumption of constant U is reasonable, because the velocity affected by the surfactant is not the

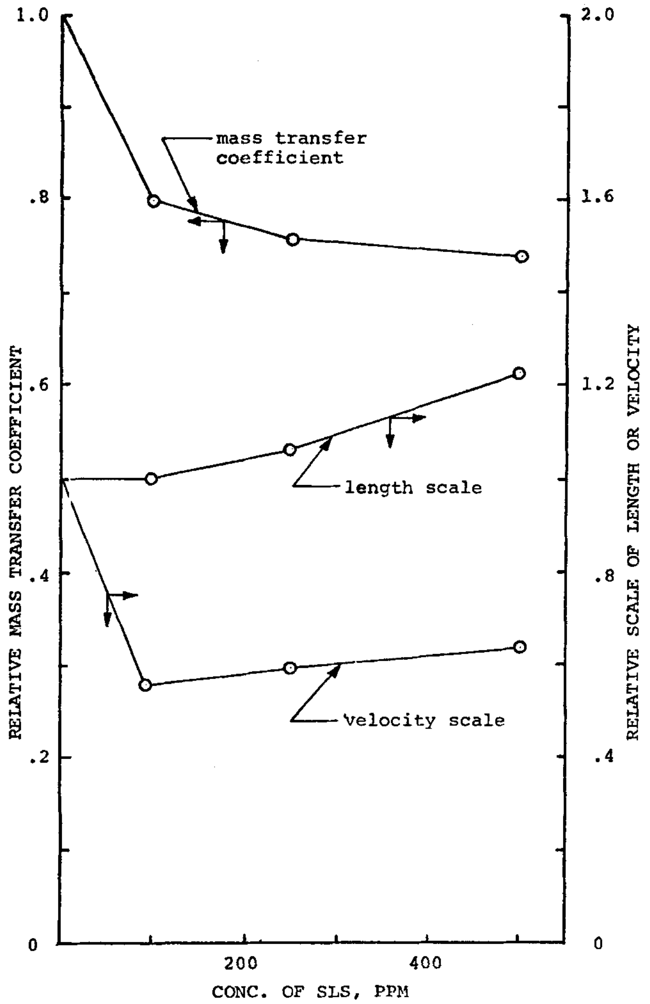

Figure 7. Relative values of k_L, L, and V vs. surfactant concentrations for SLS at 150 RPM (V and L: 100 μm below surface).

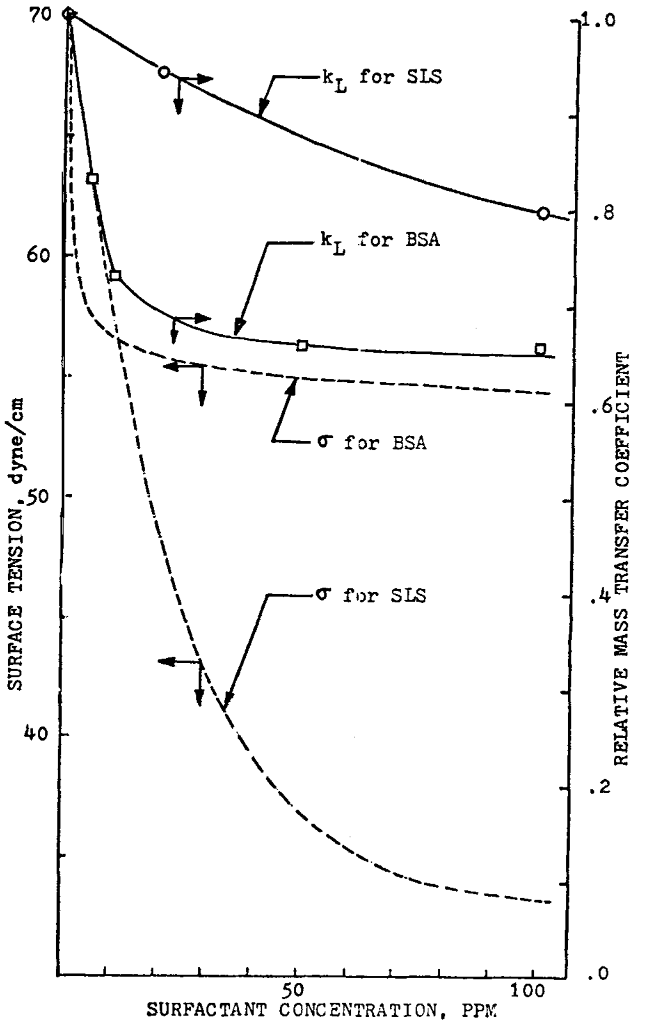

Figure 8. Surface tension and k_L vs. surfactant concentrations (150 RPM).

one parallel to the surface (i.e., U), but the one from the bulk to the surface (i.e., eddy velocity, V).

The velocity scale, V, of the liquid eddies was estimated indirectly from the existing model of the following form:

$$k_L = c_1 \sqrt{D_o V / L} \tag{5}$$

where c_1 is a constant which varied among investigators but is close to unity. The correlation of the form given in Eq. 5 appeared recently (Fortescue and Pearson, 1967; Brumfield, 1977). From Eqs. 4 and 5, the following expression was obtained:

$$\frac{V_s}{V_o} = \frac{(k_L)_s^2 T_s}{(k_L)_o^2 T_o} \tag{6}$$

Equations 4 and 6 were used for estimating the effect of surfactant on interfacial hydrodynamics. Note, however, that the velocity scale used in this study corresponds to the "equivalent" rather than the actual V, since it was evaluated indirectly.

RESULTS AND DISCUSSION

The relative values of k_L, L and V vs. surfactant concentration are given in Figures 6 and 7. It is shown that the decrease in k_L was caused by two effects: an increase in L and a decrease in V. For the macromolecular surfactants (BSA and GO), both L and V were about equally affected; whereas, for SLS, the decrease in velocity scale was more pronounced. According to Davies (1972), the eddy velocity decreases due to surface pressure exerted by the surfactants. The increase in L can be explained as follows: the reverse spreading force of the surfactant film is effective in suppressing low-energy eddies (small and slow eddies), and the resulting redistribution of eddy size caused an increase in L, which is a statistically averaged quantity.

When a single surfactant is considered, the decrease in surface tension, $\Delta\sigma$, due to the surfactant appears to have a direct relationship with the k_L reduction (Figure 8). This agrees with the observation of others (Moo-Young and Shoda, 1973). However, the same amount of $\Delta\sigma$, was shown to cause different percentage of k_L reductions for different surfactants; a $\Delta\sigma$ of 15 dyne/cm caused approximately 5% decrease in k_L for SLS, whereas k_L was reduced as much as 28% for BSA with the same $\Delta\sigma$ (Figure 8). Thus, it appears that the difference in surface tension, $\Delta\sigma$, between the clean and the surfactant-laden surface, is not appropriate for relating with k_L reduction in general.

The above discussion for $\Delta\sigma$ implicitly assumed that the surfactants recover their equilibrium surface tension immediately after the disruption by the eddies approaching the surface. In reality, there may be a time lag before the surfactant recovers its equilibrium surface tension. If so, it is not the equilibrium but the effective value of $\Delta\sigma$ that is responsible for the hydrodynamic effect. This $(\Delta\sigma)_{\text{eff}}$ is expected to depend on the properties of the surfactant. Springer and Pigford (1970) postulated that $(\Delta\sigma)_{\text{eff}}$ is related with the time constant of recovery to equilibrium for a given surfactant, and stated that a surfactant with a fast recovery time exhibits the hydrodynamic effect even at high liquid turbulence. Meijboom and Vogtlander (1974) showed that the recovery time is proportional to the gradient of surface tension with respect to the surfactant concentration, and is inversely proportional to the adsorption coefficient of the surfactant. If this approach is followed, the

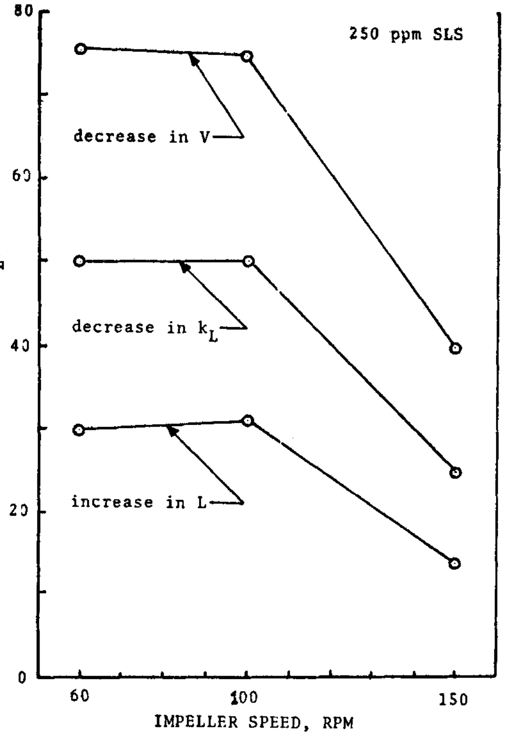

Figure 9. Changes in k_L, V, and L vs. impeller speed for SLS (V and L: 100 μm below surface).

present study shows that the macromolecular surfactants (BSA and GO) have faster recovery time compared with SLS, which has a much lower molecular weight.

The effect of impeller speed on the hydrodynamic effect is shown in Figure 9 for 250 ppm of SLS. The hydrodynamic effect decreased with increase in impeller speed. For the macromolecular surfactants, the same tendency was not clearly observable in the range of impeller speeds employed. At 60 RPM, 100 ppm of GO caused approximately 27% reduction in k_L, which was further broken down to 24% reduction in V and 42% increase in L. At 150 RPM, 100 ppm of BSA caused 39% increase in L and 40% decrease in V, which resulted in 34% decrease in k_L (Figure 6). Again, the macromolecular surfactants were shown to exert greater hydrodynamic effect compared with SLS.

Note that the surface renewal as postulated by Danckwerts (1951) was still effective even with the liquid surface covered with a surfactant. This agrees with the previous observation (Springer and Pigford, 1970). The analysis of the hydrodynamic effect by Eqs. 4 and 6 was essentially based on this premise. The small penetration assumption, often used for determining the boundary condition for gas absorption, seems to be valid, since the measured concentration boundary layer was extremely thin even at low RPM.

The hydrodynamic effect of surfactants can be used in interpreting the oxygen absorption enhancement for systems involving respiratory enzymes or aerobic microbial cells. For such systems, the increased eddy exposure time due to the hydrodynamic effect is expected to enhance oxygen absorption beyond the level of simple chemical absorption. This was observed by Lee and Tsao (1972) for oxygen absorption into glucose solution. Of course, the magnitude of the enhancement depends on the reaction kinetics and the liquid hydrodynamics. If the reaction rate due to the biologically active surfactant is negligible, the hydrodynamic effect will dominate and the mass transfer coefficient is expected to decrease even lower than that of a clean system.

ACKNOWLEDGMENT

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NOTATION

c = concentration of dissolved oxygen
c_i = concentration at the interface
c_b = concentration in the bulk
c_1 = constant
D_o = oxygen diffusivity in liquid
k_L = liquid phase mass transfer coefficient
L = length scale of eddy
$R(\tau)$ = autocorrelation coefficient
T = average period of fluctuation
U = average liquid velocity parallel to the surface
V = equivalent velocity scale of eddy
x = distance from the surface of liquid
$\Delta\sigma$ = difference in surface tension between clean surface and surfactant-covered surface
τ = time lag

Subscripts

o = without surfactant
s = with surfactant

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