Laboratory Experiment #1
Volumetric Mass Transfer Coefficient
BCHE 8210

Introduction

Mass transfer in the context of biological reactors typically involves the transport of a gaseous species such as oxygen from a gas phase to a liquid phase. The rate at which gas dissolves in a liquid (flux) at any particular time is proportional to the difference between the equilibrium concentration and the concentration at that time. A departure from equilibrium can be considered a "driving force" for mass transfer. When the equilibrium concentration is reached, the liquid is *saturated* with the gas. Under this condition, no additional gas will dissolve, and the rate of transfer is therefore zero. If the liquid is devoid of dissolved gas, then the rate of dissolution will be at a maximum. We'll come back to this point. The proportionality between the concentration difference and the transfer rate is called a mass transfer coefficient.

A simple approach is to consider two important resistances to mass transfer from a gas to a liquid: a gas film and a fluid film. The most convenient type of mass transfer coefficient is an overall mass transfer coefficient (K), which encompasses both film resistances and uses both liquid phase and gas phase concentrations in calculating an overall driving force. For gases like oxygen which are sparingly soluble in water, the liquid film is the principal resistance to mass transfer, and the overall mass transfer coefficient is approximately equal to the liquid phase mass transfer coefficient (k_L). The subscript "L" denotes that liquid phase concentrations will be used to describe the overall driving force. The concentration difference used for the driving force is the concentration of oxygen in the liquid at saturation (c^*_{O2}) and the actual liquid phase concentration of oxygen (c_{O2}). Thus, the molar oxygen flux (Φ_{O2}) can be written:

$$\Phi_{O2} = k_L \left(c^*_{O2} - c_{O2} \right) \tag{1}$$

Equation 1 can be thought of as providing a definition for the mass transfer coefficient.

Performing a mole balance in the liquid phase of a bioreactor yields:

Accumulation of O_2 = Moles O_2 In - Moles O_2 Out + Moles O_2 Generated

In the absence of microbial cells, the two terms "Moles O_2 Out" and "Moles O_2 Generated" are each equal to zero. The material balance equation thus becomes:

$$\frac{d\left(V\, c_{O2}\right)}{dt} = \Phi_{O2}\, A \tag{2}$$

where A is the surface area available for transfer and V is the system (fermentor) volume. With the system volume constant, substituting the expression of the molar flux (Equation 1) into the molar balance (Equation 2) and letting the specific exchange surface A/V equal "a" results in the following equation:

$$\frac{dc_{O2}}{dt} = k_L\, a \left(c^*_{O2} - c_{O2} \right) \tag{3}$$

The rate at which oxygen is supplied is also called the oxygen transfer rate OTR. That is, this same equation indicates how fast oxygen is being supplied to the bioreactor (e.g., units in mg/L·h):

$$\text{OTR} = k_L a \left(c^*_{O2} - c_{O2} \right) \tag{4}$$

Equation 3 may be integrated from a concentration of c_{O2}^i to c_{O2} and a time of 0 to t to yield the following equation:

$$\ln\left(c^*_{O2} - c_{O2}\right) - \ln\left(c^*_{O2} - c^i_{O2}\right) = - k_L a t \tag{5}$$

Dissolved oxygen probes which are used in bioreactors typically are calibrated to read "100%" when the liquid phase is saturated with oxygen at a given temperature and "0%" when oxygen is absent from the liquid phase at the same temperature. In other words, the relationship between the fractional dissolved oxygen (DO) and the actual concentrations is:

$$\text{DO} = \left(c_{O2}\right) \Big/ \left(c^*_{O2}\right) \tag{6}$$

Combining Equations 5 and 6 leads to:

$$\ln\left(1 - \text{DO}\right) - \ln\left(\frac{c^*_{O2} - c^i_{O2}}{c^*_{O2}} \right) = - k_L a t \tag{7}$$

As oxygen is dissolving in the solution, the value for DO obviously increases. Equation 7 indicates that a plot of $\ln(1 - \text{DO})$ versus time will be linear with a negative slope equal to k_La. The value of the specific exchange surface (a) is difficult to determine for small bubbles found in a bioreactor. So, the entire term "k_La" is often called the volumetric oxygen transfer coefficient (units of h^{-1}). Strictly speaking this statement is incorrect, since only the "k_L" is the mass transfer coefficient. Also, sometimes k_La is called the "overall" mass transfer coefficient. However, k_L is really just the liquid phase mass transfer coefficient, not the overall mass transfer coefficient, K_L. Calling k_L the overall mass transfer coefficient is not an egregious statement though since the values for the two mass transfer coefficients approach each other for a sparingly soluble gas, like oxygen in water. As is the common practice, in this document the term k_La will be simply referred to as the mass transfer coefficient. We now have a way to calculate the mass transfer coefficient for a certain set of physical conditions…just measure how the concentration of dissolve oxygen changes with time.

How is k_La correlated to physical parameters? The mass transfer coefficient depends on the fluid properties, type of impeller, the geometry of the bioreactor, the agitation, and the air flow conditions. For a given bioreactor with a fixed set of impellers agitating a given fluid like water, k_La can be correlated simply to agitation and air flow, typically by the following empirical relationship:

$$k_L a = \alpha (P/V)^{\beta} (U)^{\delta} \tag{8}$$

In Equation 8, P/V (e.g., units of W/m^3) is the specific power or the power-per-volume,

while U is the superficial gas velocity (e.g., units of m/h). The superficial gas velocity is equal to the volumetric flowrate of the gas divided by the cross-sectional area of the bioreactor. Both P/V and U are important parameters for scale-up of bioreactors. At small scale, typical operations have higher P/V and lower U than are usually feasible at large scale. The terms α, β, δ are empirical "constants" which depend on quite a few other system characteristics like viscosity of the fluid. (Scale up of bioreactors is made particularly challenging by other strongly interrelated factors including impeller type, impeller location, impeller number, and the effect the fluid conditions have on cells and their morphology!)

Let's reconsider that the oxygen transfer rate OTR (Equation 4) is proportional to the driving force for dissolution. As introduced in the first paragraph above, for a constant k_La as the solution approaches saturation, the rate at which oxygen dissolves slows. If the solution is already saturated with oxygen, then the OTR is zero. On the other hand, if the bioreactor is oxygen-free, then the rate of dissolving oxygen will be at its maximum possible value:

$$\mathrm{OTR}_{\mathrm{MAX}} = k_L a \left(c_{O2}^{*}\right) \tag{9}$$

If aerobic cells are present in the bioreactor, then they will be *withdrawing* oxygen at a rate, too. This rate of microbial consumption is called the volumetric oxygen uptake rate (OUR or Q_O). Imagine that very few cells are present in the bioreactor, or that those which are present are not consuming oxygen quickly. In this case, the OUR is relatively low, the rate of supplying oxygen will be able to "keep up" with the rate of oxygen withdraw, and the concentration of oxygen in the bioreactor will remain close to saturation (DO = 100%). If more cells are in the bioreactor and the OUR is comparatively high, then the consumption will tend to reduce the dissolved oxygen concentration. But remember, the lower the DO, the greater the OTR. Thus, the OUR and OTR tend to balance each other, and more specifically they tend to equalize.

The metabolism of cells is affected by the level of dissolved oxygen. At some point, the concentration of oxygen can become so low that oxygen limits aerobic metabolism. If the cells are strictly aerobic, then cell growth would become limited by the availability of oxygen. If one knows the critical oxygen concentration necessary to prevent cell growth from being limited by oxygen availability (c_{O2}^{CRIT}), then one can calculate the k_La necessary to sustain that level of oxygen for a given OUR. Specifically:

$$\mathrm{OUR} = k_L a \left(c_{O2}^{*} - c_{O2}^{\mathrm{CRIT}}\right) \tag{10}$$

In order to calculate the k_La needed to keep the culture above c_{O2}^{CRIT}, we just need to know how fast the bioreactor is consuming the oxygen (OUR). Note that cases could easily arise in dense cultures where it is simply not reasonable to have a very high OTR, and instead one is indeed forced to limit growth by oxygen or by the availability of some other nutrient. Limiting growth rate is not really a bad thing, as slowing the process slightly can have many advantages (e.g., more controlled metabolism, lower heat requirement).

The objective of this experiment is to understand how the volumetric oxygen transfer coefficient varies with operational conditions (e.g., agitation and gas flowrate).

Procedure (Note: Experiments require about 3 hours.)

Set-Up

1. Assembly of the Bioreactor
    a. Use a standard volume of water (1.60 L)
    b. Use a standard temperature (37°C)
2. Calibration of the Dissolved Oxygen Electrodes
3. For each variable studied:
    a. sparge nitrogen at a high flowrate and agitation until the DO reads zero.
    b. switch agitation off
    c. set gas flow to zero
    d. enter gas flow to desired value
    e. set agitation to desired value
    f. record time and conditions

Other Data Needed:

Diameter of Vessel: _____cm

Height of Impeller from Shaft End: _____cm

Distance between Impellers: _____cm

Length of Shaft from Headplate: _____cm

Height of Reactor: _____cm

A. Agitation Rate — Study the effect of agitation rate on the value of the mass transfer coefficient. With the air flowrate set at 1.60 L/min (1.0 vvm), perform the experiment with several agitation rates: 150 rpm, 200 rpm, 300 rpm, 400 rpm, 500 rpm, 700 rpm, 900 rpm. We are not set up to measure P/V.

B. Air Flowrate — Study the effect of air flowrate on the value of the mass transfer coefficient. With the agitation rate set at 400 rpm, perform the experiment with several air flowrates: 0.40 L/min, 0.80 L/min, 1.20 L/min, 2.00 L/min and 3.00 L/min. Convert these volumetric flowrates into superficial gas velocities.

C. Impeller Position — Use an air flowrate of 1.60 L/min. Move the upper impeller higher on the shaft so that it no longer is submerged in the water. Examine 300 rpm, 400 rpm, and 500 rpm.

D. Other variables — You may choose to investigate the effect of other parameters or conditions. For example, what is the oxygen transfer rate when there is no agitation?

E. Glycerol — Instead of using 1.60 L water, use a mixture of 20% glycerol in water (i.e., 400 mL glycerol plus 1.20 L water). Using 2 impellers and 1.60 L/min flowrate, perform experiment using 200 rpm, 300 rpm, 400 rpm, 500 rpm, 700 rpm. How does k_La compare? What has changed by using glycerol?

You should note what DO corresponds with "saturation". Visual observations can be helpful.

Report

BE ORGANIZED. The report should be written in the style of a manuscript, with an Abstract, Introduction, Materials & Methods, Results, Discussion, and References. It does not have to be lengthy, but it must be complete. Because of formatting issue which occur when figures are imbedded within text, I prefer any Tables (first in order) and Figures to appear after the References, with one Table or Figure per page. Each Table and Figure should have a number and a caption. In addition to the comments above,

1. Calculate k_La for all the experiments.

2. Plot k_La versus agitation rate. Can you find a correlation to predict how k_La varies with agitation rate (as opposed to P/V)? How do your results compare with this correlation?

3. Plot k_La versus air flowrate and with superficial gas velocity. Can you calculate the parameter δ in Equation 8?

4. How important is it to have two impellers in this fermenter when conducting an aerobic process? Do you think 3 impellers would be beneficial?

5. We just can't increase agitation of flowrate enough to get the k_La we need. The reason we want to increase k_La, though, is usually to provide a high OTR. Looking at Equation 4, how else can OTR be increased? Explain.

References

W. A. Al-Masry 1999 "Effects of antifoam and scale-up on operation of bioreactors, Chemical Engineering and Processing," 38(3):197-201.

B. Bandyopadhyay, A. E. Humphrey 1967 "Dynamic measurement of the volumetric oxygen transfer coefficient in fermentation systems," 9:533-544.

C. M. Cooper, G. A. Fernstrom, S. A. Miller 1944 "Performance of agitated gas-liquid contactors," Industrial and Engineering Chemistry, 36:504-509

F. H. Deindorfer, E. L. Gaden, Jr. 1955 "Effects of Liquid Physical Properties on Oxygen Transfer in Penicillin Fermentation," Applied Microbiology, 3:253-257.

F. Garcia-Ochoa, E. Gomez Castro, V. E. Santos 2000 "Oxygen transfer and uptake rates during xanthan gum production," Enzyme and Microbial Technology, 27(9):680-690.

P. González-Tello, F. Camacho, G. Blázquez 1994 "Density and viscosity of concentrated aqueous solutions of polyethylene glycol," 39:611-614.

G. Ruchti, I. J. Dunn, J. R. Bourne 1981 "Comparison of Dynamic oxygen electrode methods for the measurement of K_La," Biotechnology and Bioengineering, 23:277-290.

H. Taguchi, A. E. Humphrey 1966 "Dynamic measurement of the volumetric oxygen transfer coefficient in fermentation systems," Journal of Fermentation Technology, 44:881-889.

H. Tanaka 2000 "Technological problems in cultivation of plant cells at high density," Biotechnology and Bioengineering, 67(6):775-790.

M. Tobajas, E. Garcia-Calvo 2000 "Comparison of experimental methods for determination of the volumetric mass transfer coefficient in fermentation processes," Heat and Mass Transfer, 36(3):201-207.

C. A. Tribe, C. L. Briens, A. Margaritis 1995 "Determination of the volumetric mass transfer coefficient k_La using the dynamic 'gas out-gas in' method: analysis of errors caused by dissolved oxygen probes," Biotechnology and Bioengineering, 46(4):388-392.

W. S. Wise 1951 "The measurement of the aeration of culture media," Journal of General Microbiology, 5:167-177.