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NOTE

EFFECT OF OXYGEN ELECTRODE RESPONSE ON $K_L a$ MEASUREMENT

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Abstract—A study on the effect of oxygen electrode response on $K_L a$ measurement was carried out by simulation. As oxygen electrode response time increases, the estimated $K_L a$ decreases when we did not consider the electrode response time. And $K_L a$ estimation by slope method is closer to real one than curve fitting method.

INTRODUCTION

The volumetric mass transfer coefficient ($K_L a$) in gas-liquid dispersions has always played a central role in the design and characterization of bioreactor for aerobic processes. It determines the amount of oxygen that can be supplied to the liquid phase where chemical and biochemical reactions requiring oxygen are going on. The coefficient is a function of the agitation speed, gas flow rate, geometrical properties of the vessel and the agitator and, finally, of physicochemical properties of the liquid. Although some relationships between the important variables are already known, the overall process is very complex and it is not possible to obtain precise quantitative values for the coefficient of the given reactor. By far the most widely used and accepted method is the dynamic method[1], which requires the use of a dissolved oxygen electrode. The experimental procedure is reasonably straight forward. A step change is established in the oxygen concentration of the inlet gas phase and the response of the dissolved oxygen electrode is recorded. With an appropriate mathematical description of the physicochemical phenomena of the experiment, we can estimate $K_L a$ from the experimental data.

THEORY

When we consider both gas phase and liquid phase dynamics for oxygen transfer in a continuous completely mixed tank fermentor where microbial biomass consumes a constant amount of oxygen per unit time, the governing mass balance equations based on the liquid volume are [2]

$$\frac{dC_g}{dt} = \frac{1}{t_g}(C_{gi} - C_g) - K_L a \frac{1-\epsilon}{\epsilon}(C_L^* - C_L) \quad (1)$$

$$\frac{dC_L}{dt} = K_L a (C_L^* - C_L) - R + D(C_{Li} - C_L) \quad (2)$$

where t_g is the average gas residence time which is given as $t_g = (V_L/Q_g)\cdot[\epsilon/(1-\epsilon)]$, and R represents the microbial oxygen uptake rate.

If the dimensionless variables X, Y, λ and t^* are defind as [3]

$$X = \frac{C_g - C_g^1}{C_{gi}^2 - C_{gi}^1}, \quad Y = \frac{C_L - C_L^1}{C_L^{2*} - C_L^{1*}} \quad (3)$$

$$\lambda(C_g^2 - C_g^1) = (C_L^{2*} - C_L^{1*}) \quad (4)$$

$$t^* = t/t_g \quad (5)$$

where λ is dimensionless solubility of oxygen, equations (1) and (2) can be rewritten in dimensionless forms:

$$\frac{dX}{dt^*} = 1 - X - a_1(X - Y) \quad (6)$$

$$\frac{dY}{dt^*} = a_2(X - Y) - a_3 Y \quad (7)$$

$$X = 0, Y = 0 \quad \text{at} \quad t^* = 0, \quad (8)$$

$$a_1 = K_L a t_g \lambda \frac{1-\epsilon}{\epsilon}, \; a_2 = K_L a t_g, \; a_3 = D t_g. \quad (9)$$

Then the liquid phase oxygen concentration is given by[4]

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$$Y(t)=Y(\infty)\,[1-\alpha\exp(m_1t^*) - (1-\alpha)\exp(m_2t^*)] \quad (10)$$

$$m_1=\frac{-q_1+\sqrt{q_1^2+4q_2}}{2},\quad m_2=\frac{-q_1-\sqrt{q_1^2+4q_2}}{2} \quad (11)$$

$$q_1=1+a_1+a_2+a_3,\quad q_2=a_2+a_1a_3+a_3 \quad (12)$$

$$\alpha=-\frac{m_2}{m_1-m_2} \quad (13)$$

Usually $-m_2$ is at least one order of magnitude larger than $-m_1$. For t^* values greater than 5, only the first exponential term is significant so that

$$Y(t^*)=Y(\infty)\,[1-\alpha\exp(m_1t^*)] \quad (14)$$

Therefore, a semilogarithmic plot of $1-Y(t^*)/Y(\infty)$ yields a straight line with a slope of m_1 when t^* becomes large. From m_1 we can deduce K_La

$$K_La t_g=\frac{-m_1(a_3+1)-(m_1^2+a_3)}{(1+\frac{1-\epsilon}{\epsilon}\lambda a_3)+m_1(1+\frac{1-\epsilon}{\epsilon}\lambda)} \quad (15)$$

when $a_3=0$, equation (15) reduces to

$$K_La t_g=\frac{m_1-m_1^2}{1+m_1(1+\frac{1-\epsilon}{\epsilon}\lambda)} \quad (16)$$

If we employ an oxygen electrode to measure dissolved oxygen concentration, the oxygen electrode response can be obtained by solving a related partial differential equations[5-8]. But in practice a simple first order response with some time lag has been known to adequately describe the oxygen electrode[9,10]. Then the slope obtained by equation (15) will be modified by[4,11]

$$t_e\frac{d\bar{Y}}{dt^*}+\bar{Y}=Y(t^*),\quad \text{at } t^*=0,\ \bar{Y}(t^*)=0 \quad (17)$$

where t_e is the first order time constant of the electrode. Then from equation (6), (7) and (17), the solution is

$$\bar{Y}(t^*)=Y(\infty)\{1-\exp(-\frac{t^*}{t_e})+\frac{\alpha}{1+m_1t_e}[\exp(-\frac{t^*}{t_e})-\exp(m_1t^*)]+\frac{1-\alpha}{1+m_1t_e}[\exp(-\frac{t^*}{t_e})-\exp(m_2t^*)]\} \quad (18)$$

If we take the slope of the semilogarithmic plot of $1-Y(t^*)/\bar{Y}(\infty)$ by neglecting the last term, we have

$$\frac{d\ln(1-\frac{\bar{Y}(t^*)}{Y(\infty)})}{dt^*}=\frac{-\frac{1}{t_e}\exp(-\frac{t^*}{t_e})(1-\frac{\alpha}{1+m_1t_e})+\frac{\alpha m_1}{1+m_1t_e}\exp(m_1t^*)}{\exp(-\frac{t^*}{t_e})(1-\frac{\alpha}{1+m_1t_e})+\frac{\alpha}{1+m_1t_e}\exp(m_1t^*)} \quad (19)$$

$$\text{slope}=\frac{m_1-\frac{1}{t_e}(\frac{1+m_1t_e}{\alpha}-1)\exp[(-\frac{1}{t_e}-m_1)t^*]}{1+(\frac{1+m_1t_e}{\alpha}-1)\exp[(-m_1-\frac{1}{t_e})t^*]} \quad (20)$$

When $|m_1|$ is less than $1/t_e$, the slope will approach m_1 as t^* goes to infinite. Thus theoretically K_La values from the slope will be less sensitive to the electrode response time than that from the curve fitting of the response curve in the full time domain.

RESULTS AND DISCUSSION

In Figure 1 the electrode response curves are given with varying characteristic time from equation (18) at the simulation conditions of Table 1. The data in Table 1 are obtained from the results of Chang et al.[12]. The characteristic time is defined as the electrode response time normalized with respect to the inverse of K_La to be measured. Thus CT=0 means that the

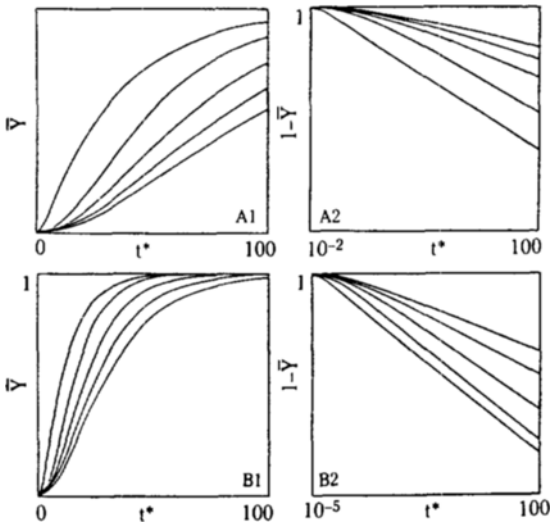

Fig. 1. Effect of time constant of dissolved oxygen electrode on the response.
(A1) $U_{sg}=1.30$, $\epsilon=0.039$, $K_La=0.0108$, $t_g=2.87$
(B1) $U_{sg}=5.74$, $\epsilon=0.135$, $K_La=0.0388$, $t_g=2.50$
From the top CT=0, 0.2, 0.4, 0.6 and 0.8, respectively. (A2), (B2): semilogarithmic plot of (A1) and (B1), respectively.

Table 1. Simulation conditions (D=0)

U_{sg}	ϵ	K_La	t_g
1.30	0.039	0.0106	2.87
5.74	0.135	0.0388	2.50

Table 2. Effect of oxygen electrode response on K_La

CT	0	0.2	0.4	0.6	0.8	TI
$K_La=0.0106$						
A	1.0	0.615	0.421	0.317	0.254	(0-28)
B	1.0	0.939	0.736	0.578	0.471	(18-28)
C	1.0	0.998	0.937	0.817	0.701	(40-65)
$K_La=0.0388$						
A	1.0	0.762	0.618	0.515	0.440	(0-28)
B	1.0	1.0	0.999	0.972	0.884	(18-28)
C	1.0	1.0	1.0	0.984	0.926	(40-65)

All estimated K_La values were normalized with respect to those of real K_La.

response is free of any distortion due to the electrode. As the characteristic time increases, the saturation of dissolved oxygen electrode response becomes slower and slower (Figure 1a). In Figure 1b the semilogarithmic plot of $(1-\bar{Y})$ versus time of Figure 1a are given. Because of the presence of the first order lag response, the slope decreases as CT increases. Also the slopes depend on the time interval chosen for the measurement as predicted by equation (20).

In real fermentation systems, dissolved oxygen electrode has a large response time constant and its time constant varies with the number of autoclaving. So we can not know the electrode response time exactly and the estimated K_L a value using equation (20) is not precise because t_e in equation (20) is not precise. In this study we assume the time constant as zero and estimate the K_La value using equation (16) from the slope of dissolved oxygen electrode response profile at the varying characteristic time and time interval to study the effects of characteristic time and the time interval on K_La value.

Table 2 shows that two real K_La values of 0.0106 and 0.0388 can be altered depending on the estimation method and the oxygen electrode response time constant and the time interval(TI). The values in Table 2 are the ratios of estimated K_La to real K_La. The estimated K_La values are obtained from the profiles of Figure 1 using equation (14) or (16). Either the increase of K_La or t_e can increase CT which is defined as the multiplication of K_La and t_e, and that decreases the estimated K_La value. So the estimated K_La will be smaller than the real one when CT>0. As a method of K_La estimation, the curve fitting method(A) using equation (14) yields K_La which are more sensitive to the CT than the slope method. When the slope method (B, C) using equation(16) is employed, K_La is less sensitive to the CT than the curve fitting (Powell's) method[13] and it closes to the real one at the later TI. That is shown in a column of Table 2. The values of B and C in a column are greater than that of A when $CT \neq 0$. This shows the feasibility of slope method when we estimate K_La without knowing t_e. The value of C is greater than that of B in a column. This means that the later time interval has less electrode response time effect than the earlier time interval. This effect can be seen in equation (20). However, the theoretical prediction applies only to the results for a late time.

In practice, the influence of the electrode is unavoidable, it is severer when K_La is larger, and as a result a smaller K_La is obtained unless a proper correction is made with respect to the time constant. However, error can be minimized by using an electrode with smaller time constant and also by taking the slope at the time interval with later TI.

Conclusively, the increase of dissolved oxygen electrode response time decreases the estimated K_La when we do not consider the response time effect. And K_La estimation by slope method at later TI closes to real one than curve fitting method.

NOMENCLATURE

a_1, a_2, a_3 : dimensionless coefficient defined in equation (6)
C_g : gas phase oxygen concentration [mol/L]
C_g^1 : gas phase oxygen concentration of state 1 [mol/L]
C_{gi} : gas phase oxygen concentration at inlet [mol/L]
C_{gi}^1, C_{gi}^2 : gas phase oxygen concentration at inlet of state 1 and 2 [mol/L]
C_L : liquid phase oxygen concentration [mol/L]
C_L^1 : liquid phase oxygen concentration of state 1 [mol/L]
C_{Li} : liquid phase oxygen concentration at inlet [mol/L]
C_L^* : liquid phase oxygen concentration in equilibrium with gas phase [mol/L]
C_L^{1*}, C_L^{2*} : liquid phase oxygen concentration in equilibrium with gas phase of state 1 and 2 [mol/L]
CT : dimensionless time constant of an oxygen electrode [$t_e \cdot K_La$]
D : dilution rate [1/s]
K_La : volumetric mass transfer coefficient [1/s]

m_1, m_2 : dimensionless coefficient defined in equation (8)
Q_g : gas flow rate [L/s]
q_1, q_2 : dimensionless coefficient defined in equation (9)
R : microbial oxygen uptake rate [mol O_2/L·s]
t : time [s]
t_e : first order time constant of oxygen electrode [s]
t_g : gas residence time [s]
t^* : dimensionless time [t/t_g]
TI : dimensionless time interval used to evaluate a slope
U_{sg} : superficial gas velocity [cm/s]
V_L : total fermentor volume [L]
X : dimensionless gas phase oxygen concentration $[(C_g-C_g^1)/(C_{gi}^2-C_{gi}^1)]$
Y : dimensionless liquid phase oxygen concentration $[(C_L-C_L^1)/(C_L^{2*}-C_L^{1*})]$
$\bar{Y}$: dimensionless liquid phase oxygen concentration measured by dissolved oxygen electrode

Greek Letters

α : dimensionless coefficient defined in equation (10)
ϵ : gas holdup
λ : dimensionless oxygen solubility

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