DETERMINATION OF THE AERATION CAPACITY OF BUBBLE COLUMNS BY DYNAMIC METHOD. THE INFLUENCE OF AXIAL DISPERSION AND OF THE START-UP PERIOD

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A dynamic method for the determination of volumetric mass transfer coefficient of oxygen, k_La, in bubble columns using an oxygen electrode was derived on the basis of a liquid phase axial dispersion model. The influence of aeration startup was studied assuming that the k_La value is position and time dependent. The conditions are defined under which the influence of aeration startup and of axial mixing of the liquid upon the steady state k_La value is negligible. A critical assessment has been made of various methods proposed for evaluation of oxygen probe responses.

Gas buble columns are simple and inexpensive absorption devices which are used ever more widely for aerobic fermentation. Batch operation with respect to the liquid as well as cocurrent or countercurrent flows of gas and liquid are possible. In these columns, the linear velocities of liquid tend to be very small, and this is why it is usually assumed that rapid back-mixing of liquid maintains a nearly uniform liquid concentration throughout the column, even in columns having large height-to-diameter ratios. Axial mixing of the liquid phase was thoroughly studied[1]. Axial mixing of the gas phase is not intensive at low gas flow rates, owing to a tendency of the rising bubbles to concentrate near the axis of apparatus.

The rate of the biosynthesis effected in this type of apparatus is often limited by the rate of oxygen transfer between the gas and the liquid. The data on the gas–liquid mass transfer are not abundant in literature. Correlations of the volumetric mass transfer coefficient presented by Akita and coworkers[2,3] are recommended[4] for estimation of the aeration capacities of apparatus of this kind. To measure k_La, Akita and coworkers used the sulfite method[5] and also the dynamic method[2] based on monitoring non-steady state oxygen absorption after an abrupt reactivation of aeration in a batch which previously was stripped of all its dissolved oxygen. The application of the sulfite method is risky, inasmuch as the accompanying chemical reaction between dissolved oxygen and SO_3^{2-} ions may bring about an unidentified increase of the mass transfer coefficient with respect to its value in physical absorption[6,7]. The dynamic method is universal and technically simple, especially when an oxygen probe is used to follow the oxygen concentration changes in the batch.

It is usually assumed in applying the dynamic method that a steady state volumetric mass transfer coefficient is attained immediately on resumption the batch aeration. In reality, a certain period of time – the so-called start-up period – is necessary to bring enough gas into the apparatus to attain steady state gas holdup and, thus, steady state interfacial area of dispersion. The effect of the start-up period on the k_La value measured by a dynamic method in mechanically agitated vessels has been studied elsewhere[8–10].

This paper presents a similar study of the effect of the startup period on dynamic k_La determination in bubble columns. The treatment involves both the effect of longitudinal mixing and the dynamics proper of the probe.

THEORETICAL

Consider a batch arrangement for the liquid phase and a through-flow for the gas phase. It is assumed that the axial dispersion of liquid is described by a model of the axial dispersion and that either the gas phase is ideally mixed or that the oxygen concentration change along the column is negligible. Then the differential balance of oxygen in the liquid can be written as

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} + k_La(mp_k - c)\,, \qquad (1)$$

where p_k is the oxygen partial pressure in outgoing gas. At first the liquid phase contains no dissolved oxygen,

$$c(0, x) = 0\,. \qquad (2)$$

The volumetric mass transfer coefficient is not constant but gradually changes from zero when aeration is started to a steady state value k_La^0. We assume that k_La^0 is reached just at the time τ when the bubbles rising through the column at a translating velocity u_g reach the surface level of liquid, $\tau = L/u_g$. It means that k_La depends on time and position as follows:

$$k_La = k_La^0\, \delta(u_gt - x)\,. \qquad (3)$$

During the startup period, *i.e.*, at $t \leqq \tau$, the circulation of liquid due to the motion of bubbles is not yet fully developed. Therefore, we assume that in the startup period the coefficient of axial dispersion is zero:

$$D = 0 \quad \text{for} \quad t \leqq \tau\,. \tag{4}$$

Eqs (*1*) through (*4*) yield the time dependence of the oxygen concentration profile in the liquid phase during the startup period. In a dimensionless form we have

$$Z(X, T) = \exp\left[-(T - XA)\,\delta(T - XA)\right] \quad \text{for} \quad \begin{cases} T \leqq A \\ (t \leqq \tau) \end{cases}, \tag{5}$$

where

$$X = x/L\,, \quad T = t\,k_L a\,, \quad Z = 1 - c/(mp_k)\,, \quad A = \tau\,k_L a^0\,. \tag{6}$$

For $T = A$ this relation gives the initial condition for the solution of Eq. (*1*) just after the startup period has ended:

$$Z(A, X) = \exp\left[-(1 - X)\,A\right]. \tag{7}$$

Neglecting the interfacial mass transfer of oxygen across the surface level into the liquid we obtain the following boundary conditions:

$$\begin{aligned} \partial c/\partial x &= 0 \quad \text{for} \quad x = 0\,, \\ \partial c/\partial x &= 0 \quad \text{for} \quad x = L\,. \end{aligned} \tag{8}$$

The dimensionless solution of the equation (*1*) with boundary conditions (*8*) and initial condition (*7*) can be written as

$$Z = A^{-1} \exp\left[-(T - A)\right] \left\{1 - \exp(-A) + 2 \sum_{n=1}^{\infty} \cos(n\pi X)\,. \right.$$

$$\left. .\, \frac{(-1)^n - \exp(-A)}{1 + (n\pi/A)^2} \exp\left[-n^2 \pi^2 B(T - A)\right]\right\} \quad \text{for} \quad T \geqq A \tag{9}$$

where

$$B = D/(k_L a^0 L^2)\,. \tag{10}$$

For illustration, Fig. 1 shows the time dependences of dimensionless oxygen concentration given by Eqs (*5*) and (*9*) for $A = 0{\cdot}3$ and for several values of B at the bottom ($X = 0$), at the surface level ($X = 1$), and in the middle of the liquid height ($X = 0{\cdot}5$). For stagnant ($B = 0$) of for ideally mixed ($B \to \infty$) liquid the slope of the dependence of ln Z against T equals unity after the startup period. Hence, for these cases, the slope of the logarithm of true concentration at a given position inside the column is equal to the steady state value of volumetric mass transfer coefficient, $k_L a^0$. For B not equal to 0 or ∞ the slope of the dependence of ln Z against T differs from unity. These differences grow with increasing distance from $X = 0{\cdot}5$. The range in which the time dependence of concentration can be taken as exponential is defined by the quantity Z_{max}, *i.e.*, the maximum value of Z for which the slope of the line connecting the points (Z_{max}, T_{max}) and $(Z = 0{\cdot}1, T = T_{0.1})$ in semilogarithmic coordinates differs by 5% from unity,

$$\left|(\ln Z_{max} - \ln 0{\cdot}1)/(T_{max} - T_{0.1}) - 1\right| = 0{\cdot}05\,. \tag{11}$$

The values of Z_{max} evaluated from Eqs (*9*) and (*11*) are shown in Fig. 2 as a function of A and B. For $Z \leqq Z_{max}$ it can be assumed that the concentration is an exponential function of time,

$$Z = \exp\left[-(T - T_0)\right], \tag{12}$$

where T_0 is the shift induced by the startup period.

If the time dependence of oxygen concentration is measured by an oxygen probe, the probe reading can be distorted due to unsteady diffusion of oxygen through the

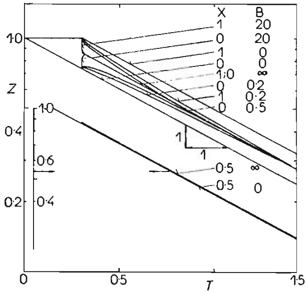

FIG. 1

Time Dependence of the Dimensionless Concentration Z at Various Locations in the Column for $A = 0{\cdot}3$ and for Various Values of B Calculated from Eqs (*5*) and (*10*)

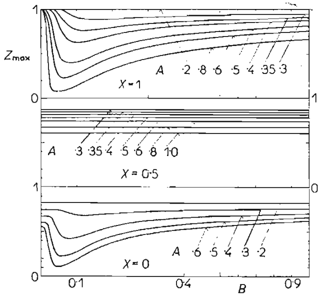

FIG. 2

The Value of Z_{max} as a Function of Value A and B

liquid film before the probe membrane, through the membrane, and through the electrolyte layer between the membrane and the probe cathode. The probe reading can also be distorted if bubbles are present near the probe tip; this is discussed further on.

For a normalized probe response G to an exponential concentration change (*12*) the following relation was derived[11] for the case of probe covered with a membrane of uniform thickness:

$$G = 1 + 2(H + 1)\left[\exp\left[-(T - T_0)\right] \sum_{n=1}^{\infty} \frac{q_n}{u/y_n - 1} + \frac{q_n \exp\left[-y_n(T - T_0)/u\right]}{y_n/u - 1}\right] \qquad (13)$$

where

$$u = k_L a^0/k\,, \quad y_n = (\beta_n/\pi)^2\,, \quad q_n = \beta_n/\left[(H + H^2 + \beta_n^2)\sin\beta_n\right], \qquad (14), (15)$$

and β_n are positive roots of equation

$$\beta \operatorname{cotan} \beta = -H\,. \qquad (16)$$

The influence of the liquid film before the probe membrane is quantified by the parameter H. This can be determined[11] from steady state probe readings in air M_g, in nitrogen M_n, and in air saturated water M_1 under the same hydrodynamic conditions as are encountered during the measurement proper,

$$H = (M_1 - M_n)/(M_g - M_1)\,. \qquad (17)$$

The probe constant k can also be determined by an independent experiment from the transient probe characteristics measured in the gas phase. For the transient characteristics the relation derived[8,9] is

$$G^1 = 1 + 2\sum_{n=1}^{\infty}(-1)^n \exp(-n^2 kt)\,. \qquad (18)$$

EXPERIMENTAL

The apparatus is shown in Fig. 3. The bubble column of 0·1 m in diameter contained a batch 0·75 m high. The gas was distributed by a perforated plate, of which 0·12% were 52 apertures having $5 \,.\, 10^{-4}$ m in dimater. A draft tube of 0·06 m I.D. and 0·49 m high was used. The batch temperature was maintained within 22 ± 0·1°C by cooling coils.

Air was absorbed medium; its flow rate was $8{\cdot}33 \,.\, 10^{-5}$ to 10^{-3} $m^3\,s^{-1}$. Distilled water was the liquid phase. Dissolved oxygen was removed from the batch by a stream of nitrogen before the experiment. The oxygen concentration in the batch was followed by a polarographic type oxygen probe with a polyethylene membrane 15 μm thick. The probe design is shown in Fig. 4*c* of ref.[12] (Čerkasov type probe[18]). The probe was introduced at two points: *c.* 0·05 m below the batch surface level, with its cathode facing downwards (position *1*) and horizontally at *c.* 0·02 m above the bottom edge of the draft tube (position *2*), Fig. 3. The probe in the position *2* was used at air flow rates up to $4{\cdot}17 \,.\, 10^{-4}\ \mathrm{m^3\ s^{-1}}$. Practically no bubbles which might influence the probe reading were present in this location unless the flow rate exceeded the above value. At higher air flow rates the bubbles were circulating even above the tip of the probe thus placed.

The effect of bubble on the steady state probe reading (in the position *1*) was studied in a series of experiments carried out in a 0·5M sodium sulfite solution at pH 8·3 containing 10^{-4} kmol $CoSO_4$ per m^3. Under these conditions the accompanying chemical reaction is fast enough to maintain a zero oxygen concentration in the liquid[13–18]. To screen off the probe from bubbles a flat wire screen was used (wire thickness $7 \,.\, 10^{-4}$ m, mesh size $1{\cdot}5 \,.\, 10^{-3}$ m, total area $9 \,.\, 10^{-4}\ \mathrm{m^2}$, Fig. 3). The wire screen, placed at a distance of 0·01 m in front of the probe in some of the experiments, prevented the bubbles from impinging directly against the probe membrane. The transient characteristics of the probes used were determined in the gas phase. The parameter H was calculated from the probe readings in nitrogen M_n, air M_g, and the air saturated liquid, M_1, contained in the column as a function of the air flow rate using Eq. (*17*). Owing to a pronounced temperature dependence of the probe readings all these media must have the same temperature. The calculated H values are listed in Table I.

The over-all gas holdup was determined as the volume of liquid that had to be discharged from the batch if the impounded surface of the bubbled batch were to return to its original level, *i.e.*, with no gas passing.

TABLE I

Values of Certain Quantities as a Function of the Gas Flow Rate

The k_La^0 values were determined by a regression method.

$u_{sg} \,.\, 10^2$ $\mathrm{m\ s^{-1}}$	H	A	B	Z_{max}		$k_L{}^0a \,.\, 10^2$, $\mathrm{s^{-1}}$	
				$X = 0{\cdot}5$	$X = 1$	$X = 0{\cdot}5$	$X = 1$
1·06	38	0·19	0·51	0·91	1·0	2·34	2·39
2·12	60	0·24	0·28	0·89	0·96	4·01	4·78
3·19	98	0·33	0·19	0·85	0·82	6·48	7·23
4·25	109	0·34	0·17	0·85	0·80	7·69	8·40
5·31	120	0·32	0·15	0·86	0·84	9·13	9·73
6·37	120	0·31	0·14	0·86	0·86	10·6	
7·43	120	0·30	0·13	0·86	0·88	11·2	
8·50	120	0·32	0·12	0·86	0·86	12·6	
9·56	120	0·29	0·12	0·87	0·91	13·0	
10·6	120	0·28	0·12	0·87	0·93	13·9	
11·7	120	0·24	0·13	0·88	0·95	13·6	
12·7	120	0·21	0·13	0·90	0·96	13·2	

RESULTS AND DISCUSSION

Effect of Bubbles on the Probe Reading

In probes placed in gas–liquid dispersions, direct contact may occur between the bubbles and the probe membrane. Usually, it is assumed that the probe reading corresponds to the oxygen concentration in the liquid. If the oxygen concentration in gas is not in equilibrium with that in liquid, the probe reading may be affected by such contact[10]. Efforts have been made[13] toward quantifying this effect on the basis of local gas holdup ε:

$$M = \varepsilon M_g + (1 - \varepsilon) M_l \,. \qquad (19)$$

Experimental results[14] obtained in a mechanically agitated bubble reactor showed that the expression (*19*) is inadequate. This is due to the fact that it is not based on the mechanism proper of the bubble-membrane contact[14]. Our investigation into the validity of Eq. (*19*) gave similar results: Fig. 4 shows the probe reading in the position *1* (below the surface level) as a function of the superficial gas flow rate in a sulfite

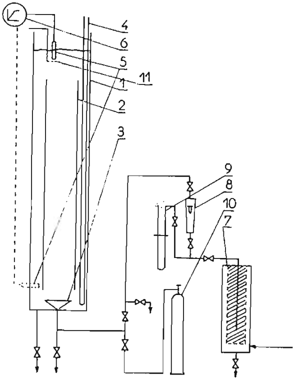

FIG. 3

Sketch of Apparatus

1 Glass cylinder, 2 draft tube, 3 gas distributor, 4 heat exchanger, 5 oxygen probe, (possition *1* on top, position *2* at bottom), 6 recorder, 7 air filter, 8 rotameter, 9 U manometer, 10 nitrogen pressure bottle, 11 wire screen.

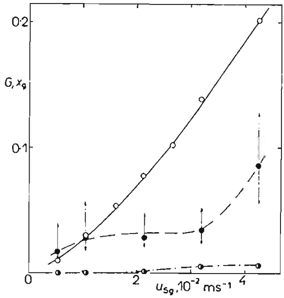

FIG. 4

Probe Reading G in the Position *1* and the Volumetric Fraction x_g of Gas Dispersion of 0·5M Sodium Sulfite Solution as a Function of the Fictive Velocity u_{sg} of Gas in Apparatus

● G Probe readings without screen, ◑ G probe readings with protective screen, ○ x_g values.

solution containing cobalt catalyst, *i.e.*, under conditions where the oxygen concentration in the liquid phase is zero. The mean volumetric fractions of gas in the dispersion, x_g, are also plotted in the figure. The probe readings (normalized with respect to readings in air, $G = M/M_g$) fluctuated about a mean value shown as a point in the figure; the fluctuation amplitude is denoted by line segment. The fraction x_g goes up with increasing gas flow rate. The dependence of the local volumetric fraction of gas in the position *1*, ε, on the gas flow rate can be expected to exhibit no substantial difference from that determined for x_g. However, it follows from Fig. 4 that the relationship between the mean volumetric fraction and the probe reading is not commensurate at all with the Eq. (*19*). When the wire screen was placed before the membrane, the probe reading did not fluctuate and was practically zero, even at high gas holdups by up to 20%. During the experiments, we have been able to follow the probe reading and, simultaneously, observe whether a bubble was stuck on the probe membrane. There was an unambiguous coincidence between bubble sticking to the membrane and the incidence of local maxima in the recorder chart. In such cases the bubbles tended to remain stuck on the membrane for 10 to 15 seconds; this was enough to allow 60 to 80% saturation of the liquid batch at higher gas flow rates. Hence, the expression (*19*) is inadequate for describing the bubble-probe interaction under the conditions of rapid saturation of the batch by oxygen. Essentially, this is due to the fact that the potential bubble sticking time is comparable with the time needed for batch saturation with oxygen, *i.e.*, with the duration of the entire experiment. The bubble-probe interaction can simply be suppressed using various procedures such as described in[14]. This is more advantageous than to develop complicated models of this effect.

Gas holdup

Our experimental gas holdups, together with data extracted from literature, are shown in Fig. 5 where the mean volumetric fraction of gas in dispersion is plotted against the fictive gas velocity u_{sg}. A good agreement has been found between our data and those by Reith[1]. However, the correlation presented by Akita[2] and recommended in a monograph[4] does not fit very well onto our or Reith's data. At high gas flow rates the correlation yields lower values (by up to 25%). Apparently, this is a consequence of an inadequate goodness of fit of the Akita correlation, since the scatter of Akita's experimental data about the correlation line proposed is substantial, too; (by up to 45% as extracted from Fig. 4 of ref.[2]). A more recent correlation suggested by Kumar and coworkers[18] fits the data better, as it is seen in Fig. 5.

Volumetric Mass Transfer Coefficient

The k_La^0 values were calculated using a nonlinear regression equation (*13*): T_0 and U were determined so as to minimize the sum of squares of the relative deviations between experimental values and those obtained from Eq. (*13*). The probe constant $k = 1{\cdot}28\ \mathrm{s}^{-1}$ was established in a similar manner from the probe response to an abrupt oxygen concentration change in gas using Eq. (*18*). To evaluate k_La^0, only those G values within the range of 0·2–0·97 were employed because, as follows from the $Z_{\max}$ values (Table I) calculated for our experiments, at values below 0·2 the startup period has a substantial effect. The $Z_{\max}$ values were read off from the diagram in Fig. 2. The appropriate values of the parameters A and B (Table I) were estimated as follows: τ was determined from the velocity of the ascending bubbles in the draft tube and from the velocity of their descent along the walls of the bubble column in the annular space; the values of the axial dispersion coefficient D were taken from ref.[1]. To illustrate the startup effect the responses of probes located in the position *1* (corresponds to $X = 0{\cdot}5$) and in the position *2* (corresponds to $X = 1$) are plotted in Fig. 6 starting from the instant when air was let into the column. A pronounced time shift of the probe responses, due to the startup period, can be observed. The draft tube above the gas distributor directs the circulation of the dispersion so that it reaches the position *2* ($X = 1$) only when circulating back. This is why a double batch height was substituted for L in evaluating A and B. It has been ascertained that the time dependence of ln G was linear for some other G values laying below

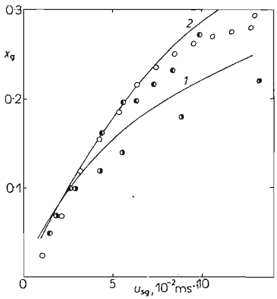

FIG. 5

Volumetric Fraction x_g of Gas in Aqueous Dispersion as a Function of Velocity u_{sg} ○ Our data, ◐ Reith[1] data for d 0·0508 m, L 2 m; ◑ Reith[1] data for d 0·1 m, L 3·53 m, line *1*: Akita's correlation[2] of our and Reith's data[1]; line *2*: Kumar correlation[15] of our and Reith's data[1].

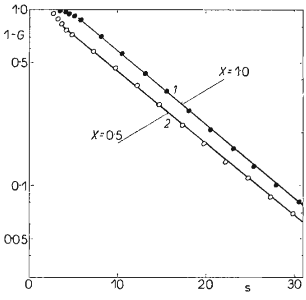

FIG. 6

Normalized Probe Responses for Probes Placed in the Positions *1* and *2* at $u_{sg} = 5{\cdot}31 \cdot 10^{-2}\ \mathrm{ms}^{-1}$ Recorded from the Instant when Air Was Introduced into the Column (○ position *1*, ● position 2) the value corresponding to Z_{max}. This is due to the fact that the condition *(4)* of a zero axial dispersion during the startup period is too strict. In reality, some axial mixing of the liquid batch takes place from the very instant of introducing air, even though on a limited scale. This is why the axial concentration profile formed during the startup period is not so steep as predicted by Eq. *(15)* derived from the model. However, this method has the advantage of keeping on the safe side with the calculation. In contrast, the notion expressed by Votruba and coworkers[16] about the effect of axial dispersion on the determination of the volumetric mass transfer coefficient in bubble columns by a dynamic method falls short of according the proper significance to this effect, and this *a priori* underestimation is responsible for their incorrect conclusion that this effect is unimportant in this kind of apparatus (see Appendix). Our results of k_La^0 determination are shown in Fig. 7 together with literature data; our values are in good agreement with those by Votruba and coworkers[16] which

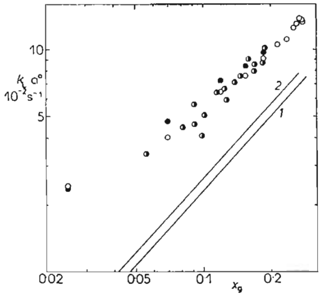

FIG. 7

Volumetric Mass Transfer Coefficient k_La^0 as a Function of Volumetric Fraction x_g of Gas in Dispersion

Our experiments with probe in position *1*, our experiments with probe in position *2*, ◑ Votruba's data[16]; Line *1* Akita's correlation of our data; line 2: Akita's correlation[2] of Votruba's data[16].

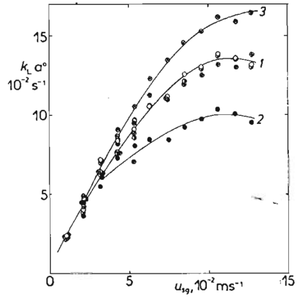

FIG. 8

Comparison of the Volumetric Mass Transfer Coefficients k_La^0 Calculated by Various Methods

Line *1*: ○ regression method *(13)*, ◑ moment method *(D3)* with origin of the time axis determined by regression, ⊕ moment method *(D3)* with origin of the time axis given by air introduction into the column. Line *2*: ● moment method *(D2)* with origin of the time axis determined by regression, ⊗ moment method *(D3)* with origin of the time axis coincident with the throw of the recorder pointer. Line *3* on the p. 2596.

had also been determined by the dynamic method (using the oxygen probe in a medium exhibiting properties not too much different from those of water). It is also clear that our data and those by Votruba and coworkers[16] do not agree with Akita's correlation[2] which, similarly as in the case of gas holdup, gives substantially lower values of the volumetric mass transfer coefficient (by up to 50%). Votruba and coworkers have stated[16] that their data do agree with Akita's correlation (Fig. 1 of their paper[16]) but this may be due to an erroneous calculation on their part. The disagreement of our and Votruba's data with Akita's correlation may in part be explained by the loose fit of the latter. Fig. 9 of Akita's paper[2] indicates a fairly large scatter of the experimental data about the correlation, the deviations reach up to 100%.

The $k_{\mathrm{L}}a^0$ values calculated from the probe readings are nearly the same for probes placed in either the position *1* or the position *2* (Table I). Those values obtained from the position *2* are by 8% higher on the average. This difference contradicts the assumption made by Votruba and coworkers[13,16,20] about the effect of holdup on the probe reading; there were no bubbles present near the electrode placed in the position *2* and thus $k_{\mathrm{L}}a$ values obtained from this position ought to be lower than those from the position *1*. In contrast, this difference can be accounted for by our model of axial dispersion with startup period. The $k_{\mathrm{L}}a$ values calculated from the reading of the probe most distant from the gas inlet (at $X = 1$) are higher than is the steady state value of $k_{\mathrm{L}}a^0$ if calculated by this model. In turn, the probe readings taken near the gas inlet may lead to lower values (Fig. 1). Hence, a position exists in the column (in the vicinity of one half of the bubble path, $X = 0{\cdot}5$) where there is a minimal distortion due to the axial dispersion of the initial distribution of concentrations as produced in the startup period.

Literature recommends the moment method for oxygen probe response evaluation. Indeed, this method allows to determine the volumetric mass transfer coefficient by very simple formulas. It follows from the very principle of this method that it is sensitive to the correct setting of the time axis origin as well as to probe reading normalization. Frequently occuring errors due to an incorrect or a superficial application the moment method are discussed in Appendix.

LIST OF SYMBOLS

a	instantaneous local specific interfacial area
a^0	steady state mean specific interfacial area
A	$= k_{\mathrm{L}}a^0\tau$
B	$= D/(k_{\mathrm{L}}a^0L^2)$
c	oxygen concentration in liquid
d	column diameter
D	axial dispersion coefficient of liquid
g	gravity constant
G	normalized probe response
G^1	normalized probe response to an abrupt concentration change

H	model parameter, Eq. (*17*)
k	probe constant
k_L	coefficient of mass transfer from bubbles
k_{Lh}	coefficient of mass transfer across surface level
L	height of dispersion in apparatus
m	equilibrium distribution coefficient
M	probe reading in dispersion
M_g	probe reading in air
M_n	probe reading in nitrogen
M_1	probe reading in air-saturated batch under given hydrodynamic conditions
N	over-all absorption rate
p_k	oxygen partial pressure in outgoing gas
q_n	$= \beta_n/[(H + H^2 + \beta_n^2) \sin \beta_n]$
t	time
T	$= tk_La^0$
u_g	ascending velocity of bubbles
u_g^+	$= u_{sg}/(\Delta\varrho\sigma g/\varrho_1^2)^{1/4}$
u_{sg}	fictive gas velocity related to free cross section of apparatus
u	$= k_La^0/k$
x	spatial coordinate
X	$= x/L$
x_g	mean volumetric fraction of gas in dispersion
y_n	$= (\beta_n/\pi)^2$
Z	$= 1 - c/(mp_k)$
β_n	positive roots of equation $\beta \cot\text{an}\, \beta = -H$
δ	Dirac function
ε	local volumetric fraction of gas in dispersion
μ_0^1	zeroth moment of probe response $G^1 := \int_0^\infty (1 - G^1)\, dt$
σ	interfacial tension of liquid phase
ϱ	density
$\Delta\varrho$	$= \varrho_1 - \varrho_g$
τ	$= L/u_g$

APPENDIX

The Influence of Axial Dispersion in the Liquid Phase on k_La^0

Axial dispersion in the liquid phase was described[16] by the same equation as Eq. (*1*). The analysis[16] differs from ours by the boundary condition for $X = 1$ ($x = L$), where instead of $\partial c/\partial x = 0$ it uses the relation

$$D \frac{\partial c}{\partial x} = k_L(mp_k - c) \quad . \tag{D1}$$

Further, instead of the variable value of k_La according to Eq. (*3*) a constant value of k_La^0 is used during the entire aeration period, *i.e.*, from startup of aeration until reaching the steady state oxygen concentration inside the broth. The condition (*D1*) describes the oxygen transfer across the liquid surface into the liquid phase. This absorption of oxygen across the liquid surface must be distinguished from the so-called "surface aeration", *i.e.*, the aeration induced by bubbles which are sucked up by the liquid surface — a phenomenon frequently occurring in mechanically agitated bubble fermentors; the effect of "surface aeration" is inherent in the k_La value. Absorption across the liquid surface can practically always be neglected with regard to the intensity of aeration of the liquid by bubbles. This may be illustrated by comparing the instantaneous rates of overall oxygen mass transfer flows into the broth from bubbles, N_b, and from the borth surface N_h:

$$\frac{N_h}{N_b} \sim \frac{k_{Lh}}{k_La^0L} \approx 10^{-4} \div 10^{-2} .$$

This holds even if we neglect the fact that the coefficient of mass transfer through the broth surface, k_{Lh}, is several times smaller than from bubbles, k_L. Typically, $k_La \sim 2 . 10^{-2}\ s^{-1}$, $L \simeq 1$ m, $k_L \simeq 10^{-4}$ ms $^{-1}$ (estimated from Calderbank's correlation[19]). However, if the physically realistic condition (*3*) were used instead of Eq. (*D1*) in the analysis[16] the term describing axial dispersion in the liquid phase would lose its sense: under such condition it would hold everywhere that $\partial c/\partial x = 0$ due to constancy of the k_La^0 value. As it stands the analysis presented[16] leads only to the trivial conclusion that the effect of axial dispersion is negligible. It is not at all surprising, since only a negligible quantity of oxygen absorbed across the broth surface, according to (*D1*), can be axially dispergated in the apparatus. Thus the analysis of an axial dispersion described by Votruba and coworkers[16] cannot contribute to our understanding of axial dispersion in real fermentors and/or absorption columns, where the axial concentration profile is induced above all by phenomena connected with aeration startup.

The Moment Method of Probe Response Evaluation

The assumption (*19*) recommended by Votruba and coworkers[16,20] for description of the interaction of the probe with bubbles in bubble columns or agitated fermentors contradicts the experimental results obtained in agitated aerated fermentors as well as in bubble columns (*cf.* the results presented in this work and in a previous paper[14]). If k_La value is evaluated by a regression method, it need not be erroneous even though the erroneous assumption (*19*) was used: when a dynamic method is used where the exponential oxygen concentration change is followed, errors can be avoided as long as the assumption is linear. Generally, any linear form

$$M = f(\varepsilon)\, M_1 + h(\varepsilon)\, M_g$$

leads (using the same notation as Votruba and coworkers[16]) to

$$K_p \frac{dY_p}{dt} + Y_p = f(\varepsilon) \exp\left(-k_La^0t\right) .$$

The right-hand side can be rewritten as $\exp\left[-k_La^0(t - t_0)\right]$, the equivalent time shift, with the same value of the slope of the appropriate dependence (being equal to the k_La^0 value). This is why our and their data, shown in Fig. 7, agree well with each other. However, the assumption (*19*) influences the k_La^0 values directly when the moment method is used: according to Votruba and coworkers[20]

$$k_La^0 = (1 - \varepsilon)/(\mu_0 - \mu_o^1) . \qquad (D2)$$

The relation (*D2*) is correct as long as the assumption (*19*) is correct. Since this assumption does not agree with experimental data, it is not surprising that the k_La^0 value evaluated by Eq. (*D2*) considerably differ from those determined by the regression method, (Fig. 8, line 2). A more complete comparison of both methods (*i.e.*, regression and moment methods) was described elsewhere[21] in detail. For the evaluation of k_La^0 the relation derived[21] was

$$k_La^0 = [\mu_0(H) - \mu_o^1(H)]^{-1} . \qquad (D3)$$

The transient characteristics of the system and of the probe (and their zeroth moment μ_0 and μ_o^1) must be determined experimentally under the same hydrodynamic conditions, *i.e.*, for the same value of the parameter H. This is usually difficult to do in the case of the probe transient characteristics which, as a rule, is determined in the gas phase or by transferring the probe from air-saturated to nitrogen-saturated water. These water solutions of air and nitrogen should be intensively agitated so that $H \rightarrow \infty$. In this case the determined value of $\mu_o^1(H \rightarrow \infty)$ has to be recalculated so as to correspond with the given value of H according to

$$\mu_o^1(H) = \frac{H + 3}{H + 1} \mu_o^1(H \rightarrow \infty) . \qquad (D4)$$

The values of k_La^0 evaluated from relations (*D3*) and (*D4*) agree well with those calculated by the regression method, (Fig. 8, line *1*).

The origin of time scale, t_0, which is determined as a regression parameter when using the regression method, must be known beforehand when the moment method is applied. In this connection it is worth mentioning that the Fig. 1 of the paper[20], where the time origin is identified by the throw of the recorder pointer, is confusing: a time origin thus chosen leads to erroneous values of k_La^0, especially at higher aeration velocities, (Fig. 8, line *3*).

It is reasonable to choose as time origin the instant of aeration startup. The k_La^0 values evaluated from Eq. (*3*) with the time origin chosen in this way agree well with the values obtained by the regression method, (Fig. 8). Similarly, these time origins are very close to those values determined by the regression method, and it were these values which were used for evaluating k_La^0 by the moment method from relations (*D2*) and (*D3*).

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