



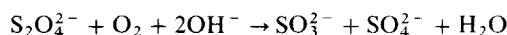
# Application of the sodium dithionite oxidation to measure oxygen transfer parameters

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**Abstract**—The oxidation of sodium dithionite with molecular oxygen in alkaline solutions takes place in two steps: in the first, dithionite oxidizes to sulphite and sulphate,



which occurs in the fast reaction regime; within this step the oxygen concentration in the bulk liquid is effectively zero and the kinetics can be followed by the decrease in the solution's reducing power or by the consumption of base required to keep the pH constant. These results allow us to determine the specific interfacial area.

In the second step, sulphite oxidizes to sulphate:

$$N_{\text{O}_2}a = -\frac{1}{2} \frac{d[\text{SO}_3^{2-}]}{dt} = -\frac{1}{4} \frac{dc}{dt}$$

which takes place in the hydrodynamic regime without catalytic agents deliberately added and allows us to determine the volumetric oxygen transfer coefficient.

However, when this method is applied using air as the gaseous phase, it leads to values of both parameters of around 90% of those that were obtained using pure oxygen. These results may be explained by the wide range of the bubble size distribution. This implies that the actual average driving-force of the oxygen transfer using air is even lower than that obtained with the approximation of perfect mixing used. © 1997 Elsevier Science Ltd. All rights reserved

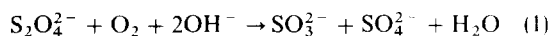
**Keywords:** Oxygen; Dithionite; Interfacial area; Transfer coefficient.

## INTRODUCTION

The low solubility of oxygen in the aqueous solutions commonly used as culture broth and the high demand for this component in aerobic fermentation processes explain the necessity for its continuous supply to the corresponding bioreactor (aeration). Thus, oxygen transfer between the gaseous phase and the culture broth becomes the limiting factor in many aerobic fermentation processes at appreciably high biomass densities, and is the greatest obstacle to increasing industrial fermentor volume in order to take advantage of the economies of scale.

For these reasons, it is of great interest to have an appropriate method available to measure oxygen transfer parameters in fermentors, mainly transfer coefficients, specific interfacial areas and bubble size distributions, to compare different bioreactor configurations and operational methods.

Therefore, using the chemical system proposed by Jhaveri and Sharma (1968), the absorption of oxygen by alkaline sodium dithionite solutions, this article describes a method that enables the determination of the specific interfacial area and the volumetric mass transfer coefficient in a stirred tank, under the same operating conditions. These results are obtained from the two successive steps that make up the oxidation of the sodium dithionite with molecular oxygen in alkaline solutions:



The kinetics of dithionite oxidation was established in previous work by our group (Camacho *et al.*, 1992, 1995), which found that, within the following ranges

$$293 \text{ K} \leq T \leq 318 \text{ K}$$

$$2 \times 10^4 \text{ Pa} \leq P \leq 1 \times 10^5 \text{ Pa}$$

$$\text{pH} \geq 8$$

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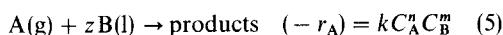
the reaction is of zero-order with respect to oxygen and 1.5 with respect to dithionite:

$$r = k[S_2O_4^{2-}]^{1.5} \quad (3)$$

with

$$k = 3.22 \times 10^5 \exp\left(-\frac{4250}{T}\right) \frac{\text{m}^{1.5}}{\text{mol}^{0.5} \text{s}} \quad (4)$$

The application of chemical methods for the determination of mass transfer parameters of gas-liquid contactors is based on the theory of simultaneous absorption with a chemical reaction in the liquid phase (Danckwerts, 1970; Charpentier, 1981),



which leads to the following expression for the volumetric flow of solute absorbed across the interface:

$$N_A a = \sqrt{1 + Ha^2} k_1^0 a (C_{A_i} - C_{A_0}) \quad (6)$$

whenever the concentration profile of reactant B in the proximity of the interface can be considered plane, which arises if

$$Ha = \sqrt{\frac{2}{n+1} \frac{D_A k C_{B_0}^m C_{A_i}^{n-1}}{(k_1^0)^2}} \ll \frac{C_{B_0}}{z C_{A_i}} \quad (7)$$

For the fast reaction regime,  $Ha \geq 3$ , volumetric flow is reduced to

$$N_A a = \sqrt{\frac{2}{n+1}} D_A k C_{B_0}^m C_{A_i}^{n+1} a \quad (8)$$

which allows the determination of the specific interfacial area,  $a$ , by experimental measuring of  $N_A a$  if the kinetic parameters of the reaction and the diffusivity and the solubility of A are known.

For the hydrodynamic regime,  $Ha \leq 0.3$ ,

$$N_A a = k_1^0 a (C_{A_i} - C_{A_0}) \quad (9)$$

which allows us to determine the volumetric coefficient,  $k_1^0 a$ , by means of experimental measurements of  $N_A a$  and  $C_{A_0}$ , when the solubility of A is known. In this case, the kinetics of the reaction does not affect the absorption process.

#### EXPERIMENTAL TECHNIQUE

The experiments were carried out in a BIOSTAT<sup>®</sup> B fermentor system (B. Braun Biotech. International). The culture vessel, with a maximum working volume of 2 litres at a total volume of 3 litres, is made of borosilicate glass and has a height/diameter ratio of 2/1.

Temperature, stirring rate, dissolved oxygen (percentage of saturation with respect to the gaseous phase), pH, alkali added and experiment time were logged by a Packard Bell computer using Micro-MFCS software (B. Braun Biotech. International).

The experiments were made on Burk's medium (González-López, 1992) as the intention was to obtain the volumetric oxygen transfer coefficient,  $k_1^0 a$ , from a particular aerobic fermentation process. The me-

dium was previously sterilized in four parts to avoid salt precipitation. The composition of 1 litre of medium was: Part I:  $K_2HPO_4$ , 0.64 g;  $KH_2PO_4$ , 0.16 g; distilled water, 100 ml. Part II: NaCl, 0.2 g;  $MgSO_4 \cdot 7H_2O$ , 0.2 g;  $CaSO_4 \cdot 2H_2O$ , 0.05 g; distilled water, 100 ml. Part III:  $FeSO_4$ , 0.003 g;  $Na_2MoO_4 \cdot 2H_2O$ , 0.001 g; distilled water, 100 ml. Part IV: sodium acetate, 2.5 g;  $NH_4Cl$ , 1 g; distilled water, 700 ml.

The operational conditions were: temperature, 30°C; stirring rate, 250 rpm and aeration 0.5 v/v/min.

The appropriate quantity of solid sodium dithionite was added to the liquid phase, previously saturated with nitrogen, and allowed to dissolve completely, adding NaOH to attain the desired pH. At this moment, samples were taken to determine the initial concentration of reducing power. The gaseous phase (pure oxygen or air) was then allowed to circulate, displacing completely the nitrogen dissolved in the initial liquid phase; at this instant, the timing of the experiment time began.

The absorption rate was measured by the change in composition of the liquid phase, which was analysed through iodometric evaluation for the total reducing power (sum of dithionite and sulphite) during both steps of the process and through the quantity of alkali added to keep the pH constant during the first step.

The physical and chemical properties were estimated as described in the article by Camacho *et al.* (1995).

#### RESULTS AND DISCUSSION

The concentrations of total reducing power, oxygen in the bulk liquid, expressed as a percentage of oxygen saturation with respect to the gaseous phase being considered, and base consumed (using air or pure oxygen as the gaseous phase) at the different pHs used (9 and 10) are plotted against time in Figs 1–4.

In these figures, the two steps of the process can be clearly seen. The first step lasted around 50 and 180 min, depending on the gaseous phase used (pure oxygen and air, respectively). During this step, the total reducing power decreased rapidly and the complete consumption of the alkali took place, while the oxygen concentration in the liquid phase was effectively zero. This step corresponds to the dithionite oxidation.

During the second step (sulphite oxidation), the rate of decrease in reducing power became virtually constant and the addition of base was ceased completely. The fact that there was a measurable concentration of dissolved oxygen indicates that the reaction takes place in the hydrodynamic regime and, therefore, that kinetics does not affect the volumetric coefficient determined. However, the different behaviour of the concentration of dissolved oxygen in the bulk liquid depending on the pH shows the high sensitivity of the sulphite oxidation kinetics, being faster at pH 9.

The dithionite oxidation (first step) in alkaline solutions with molecular oxygen within a wide interval of dithionite concentrations takes place in the fast

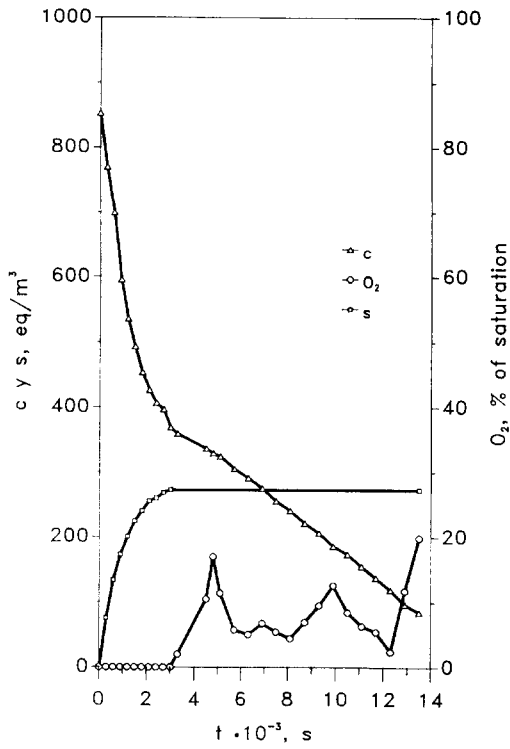


Fig. 1. Oxygen absorption at 30°C and pH = 9, using pure oxygen as the gaseous phase.

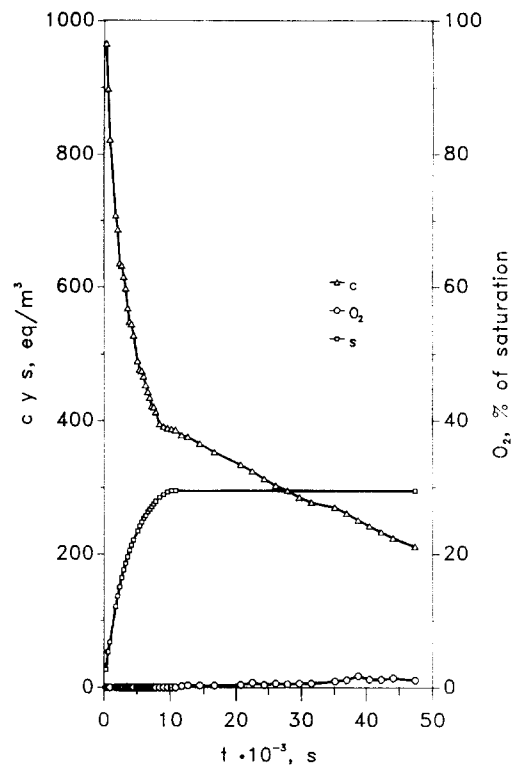


Fig. 3. Oxygen absorption at 30°C and pH = 9, using air as the gaseous phase.

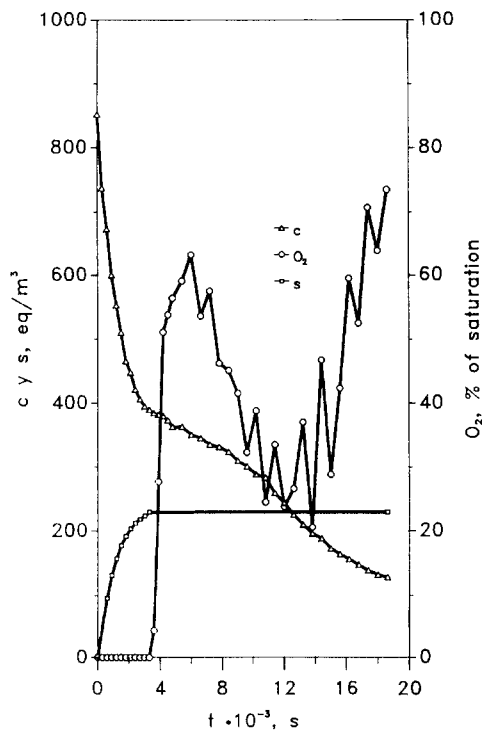


Fig. 2. Oxygen absorption at 30°C and pH = 10, using pure oxygen as the gaseous phase.

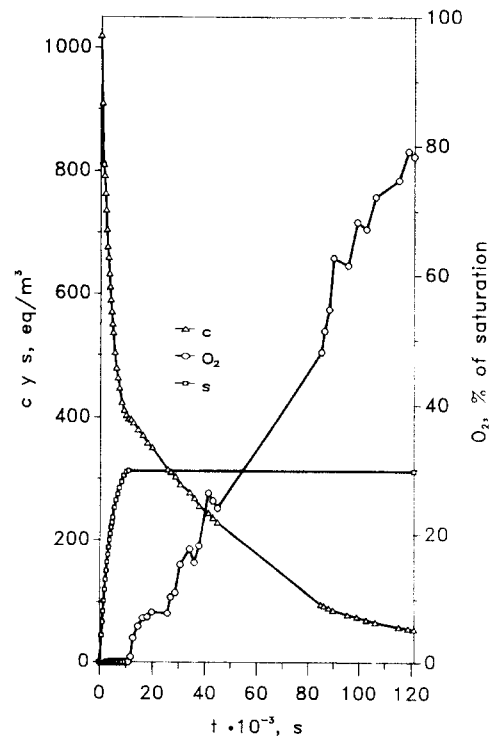


Fig. 4. Oxygen absorption at 30°C and pH = 10, using air as the gaseous phase.

reaction regime and so, taking into account eqs (3) and (8), the volumetric flow of oxygen is given by

$$N_{O_2}a = \sqrt{2kD_{O_2}[O_2]_i[S_2O_4^{2-}]^{1.5}}a. \quad (10)$$

On the other hand, from reaction (1),

$$N_{O_2}a = \frac{1}{2} \frac{ds}{dt} = -\frac{d[S_2O_4^{2-}]}{dt} = -\frac{1}{4} \frac{dc}{dt} \quad (11)$$

where  $s$  and  $c$  are the concentrations of base added and reducing power, respectively. The latter equality in eq. (11) implies that sulphite is not oxidized during the first step (dithionite oxidation); this assumption may be proven using the relationship between total reducing power and base added at each instant deduced from eq. (11):

$$c = c_0 - 2s \quad (12)$$

given that sulphite and sulphate are completely dissociated at the pHs used. The values obtained, plotting the results in the way suggested by eq. (12), are shown in Table 1.

It can be seen that the experimental results fit the prediction of eq. (12) very well; hence, the rate of disappearance of dithionite may be followed by the diminution of reducing power as well as by the consumption of base required to keep the pH constant; this latter method allows a virtually continuous monitoring of the reaction.

From eqs (10) and (11), by separating the variables and integrating:

$$[S_2O_4^{2-}]^{0.25} = [S_2O_4^{2-}]_0^{0.25} - 0.25a(2k)^{0.5} \times \int_0^t \sqrt{D_{O_2}[O_2]_i} dt \quad (13)$$

where the integral of the right-hand side allows us to take into account the small changes in the diffusivity and solubility of oxygen caused by a change in the composition of the liquid phase due to the reaction and the addition of base.

Equation (13) characterizes the first step, so that, knowing the changes in dithionite concentration with time, once the value of the kinetic constant has been calculated from eq. (3), we are able to determine the specific interfacial area from the slope of the straight line obtained by linear regression. The results are shown in Table 2, in which it may be seen that the results obtained for the specific interfacial area are approximately 10% lower when air, rather than pure oxygen, is used as the gaseous phase.

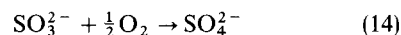
Table 1. Verification of eq. (12)

pH	Oxygen		Air	
	Slope	$r^2$	Slope	$r^2$
9	-2.06	0.990	-1.99	0.995
10	-2.06	0.997	-2.01	0.998

Table 2. Determination of the specific interfacial area

pH	Oxygen			Air		
	Slope	$r^2$	$a$ (m <sup>-1</sup> )	Slope	$r^2$	$a$ (m <sup>-1</sup> )
9	-15.5	0.999	105	-13.7	0.994	93.0
10	-15.1	0.997	103	-13.8	0.999	93.7

The initial sulphite and the sulphite formed during the first step of the process are oxidized to sulphate during the second step, in the absence of deliberately added catalysts, probably due to the action of the substances employed in the composition of the fermentation medium or of the metallic traces that are inevitable in the stirred gas-liquid contactors, following the reaction



which occurs at such a rate that the process takes place in the hydrodynamic regime, which is confirmed by the presence of a measurable concentration of oxygen within the liquid phase, and allows us to determine the volumetric mass transfer coefficient and, hence,  $k_1^0$  under the same operational conditions.

Taking into account reaction (14),

$$N_{O_2}a = -\frac{1}{2} \frac{d[SO_3^{2-}]}{dt} = -\frac{1}{4} \frac{dc}{dt} \quad (15)$$

must be observed and, as the process occurs in the hydrodynamic regime, the volumetric flow of oxygen is also given by

$$N_{O_2}a = k_1^0 a ([O_2]_i - [O_2]_0) \quad (16)$$

thus, combining the two equations, the characteristic equation of this step can be deduced:

$$c = c_1 - 4k_1^0 a \int_{t_1}^t ([O_2]_i - [O_2]_0) dt \quad (17)$$

where the initial ( $t_1, c_1$ ) corresponds to the instant at which the addition of alkali was stopped completely. The minor changes in oxygen concentration at the interface, due to the change in the composition of the liquid phase together with the oscillations in oxygen concentration in the bulk liquid, are taken into account evaluating the right-hand side integral.

A plot of the reducing power against this integral will give a straight line: its slope allows us to determine  $k_1^0 a$ , and hence  $k_1^0$  assuming the corresponding specific interfacial area calculated in the first step. The results are shown in Table 3.

As can be seen from the results given in Table 3, the process is longer using air as gaseous phase, as is to be expected, but the values of  $k_1^0 a$  are lower than those determined using pure oxygen. However, the  $k_1^0$  results obtained in air are virtually identical to those derived from the experiments with pure oxygen, which suggests that the cause of the differences lies in the values of the specific interfacial area calculated for each case. The difference can only be due to the

Table 3. Determination of the volumetric oxygen transfer coefficient

pH	Oxygen			Air		
	$k_1^0 a$ (s <sup>-1</sup> )	$r^2$	$k_1^0$ (m/s)	$k_1^0 a$ (s <sup>-1</sup> )	$r^2$	$k_1^0$ (m/s)
9	0.0101	0.999	$0.96 \times 10^{-4}$	0.00851	0.999	$0.92 \times 10^{-4}$
10	0.0106	0.998	$1.03 \times 10^{-4}$	0.00937	0.999	$1.00 \times 10^{-4}$

change in composition of the gaseous phase crossing the reactor, when air is used.

In the preceding calculations, the approximation to the perfect mixing for the gaseous phase was applied, for which it was necessary to determine the outlet molar fraction of oxygen, given by

$$Y_{O_{2\text{outlet}}} = \frac{(Q_{O_2})_{\text{outlet}}}{(Q_{O_2})_{\text{outlet}} + 0.79Q_{\text{air}}} \quad (18)$$

where the variation in the nitrogen flow across the contactor has been considered negligible, given its low solubility and that it does not react in the liquid phase.  $Q_{\text{air}}$  represents the air flow supplied to the contactor under the operational conditions:  $6.27 \times 10^{-4}$  mol/s, and  $(Q_{O_2})_{\text{outlet}}$  is the outlet volumetric oxygen flow calculated using the following expression:

$$(Q_{O_2})_{\text{outlet}} = 0.21Q_{\text{air}} - 0.002(N_{O_2}a). \quad (19)$$

Given the ionic strength of the solutions used, the system must be considered non-coalescent (Oolman and Blanch, 1986). This might lead to the highest values of  $a$  and  $k_1^0 a$ , if it implied the use of the minimum driving force of the process,  $Y_{O_{2\text{outlet}}}$ .

As shown by Midoux *et al.* (1980), the differences observed in the specific interfacial area when either pure oxygen or air are used as the gaseous phase are due to the distribution of bubble sizes.

In our opinion, the actual average driving force of the oxygen transfer process could be even lower than the outlet gas composition, if the bubble size distribution is wide. The composition of the outlet gaseous phase is mainly determined by the larger-volume bubbles which pass through the liquid phase more rapidly and show a smaller change in composition, while the actual average driving force is determined by the smaller-volume bubbles (because of their greater surface/volume ratio) which spend more time in the liquid phase and show a stronger change in composition.

In this sense, the results obtained suggest the possibility of getting information about bubble size distribution by means of experiments using pure oxygen and different nitrogen-oxygen mixtures as the gaseous phase.

#### NOTATION

$a$	specific interfacial area, m <sup>-1</sup>
$c$	total reducing power, eq m <sup>-3</sup>
$D_A$	diffusivity of A in the liquid phase, m <sup>2</sup> s <sup>-1</sup>

$D_{O_2}$	diffusivity of oxygen in the liquid phase, m <sup>2</sup> s <sup>-1</sup>
$Ha$	Hatta number
$k$	kinetic constant, mol <sup>-0.5</sup> m <sup>1.5</sup> s <sup>-1</sup>
$k_1^0$	individual mass transfer coefficient, m s <sup>-1</sup>
$k_1^0 a$	volumetric mass transfer coefficient, s <sup>-1</sup>
$N_{O_2} a$	volumetric flow of oxygen, mol m <sup>-3</sup> s <sup>-1</sup>
$[O_2]_0$	oxygen concentration in the liquid phase, mol m <sup>-3</sup>
$[O_2]_i$	oxygen solubility, mol m <sup>-3</sup>
$Q_{\text{air}}$	inlet air flow, mol s <sup>-1</sup>
$(Q_{O_2})_{\text{outlet}}$	outlet oxygen flow, mol s <sup>-1</sup>
$s$	base added, eq m <sup>-3</sup>
$T$	temperature, K
$Y_{O_{2\text{outlet}}}$	outlet molar fraction of oxygen

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