



## INFLUENCE OF pH ON THE OXYGEN ABSORPTION KINETICS IN ALKALINE SODIUM DITHIONITE SOLUTIONS

F. CAMACHO,<sup>†</sup> M<sup>a</sup>. P. PÁEZ, G. BLÁZQUEZ, M<sup>a</sup>. C. JIMÉNEZ and M. FERNÁNDEZ  
 Department of Chemical Engineering, University of Granada, 18071 Granada, Spain

(Received 11 August 1994; accepted for publication 17 November 1994)

**Abstract**—Results from experimental studies on the influence of pH within the alkaline range on sodium dithionite oxidation with molecular oxygen reveal that it is possible to follow the kinetics of the process by observation of the consumption of base needed to maintain a constant pH. Under the conditions studied (partial oxygen pressure higher than 20,260 N/m<sup>2</sup>, pH > 8, 295 K ≤ T ≤ 318 K, and a dithionite concentration higher than 0.01 M), absorption occurs by means of a reaction of zero order for oxygen and of 1.5 for dithionite while the apparent kinetic constant is independent of pH. Under these conditions the process is adequate for measuring interfacial areas in gas–liquid contactors and non-coalescent systems, although the high rate of reaction could be an important restriction for very efficient gas–liquid contactors, i.e. those with high values of *a* and *k*<sub>p</sub><sup>0</sup>. The discrepancy among results found in bibliography seems to be due to: (a) dithionite decomposition when the pH is lower than 8 which takes place when the starting alkaline solution is not sufficiently concentrated or when the pH is not kept constant by the addition of base, (b) absorption does not occur in the fast reaction regime.

### INTRODUCTION

The absorption of molecular oxygen in alkaline sodium dithionite solutions can be used to measure interfacial areas in gas–liquid contactors as has been proposed by the team of Sharma (Jhaveri and Sharma, 1968; Sahay and Sharma, 1973; Joshi and Sharma, 1977). However, for this application knowledge of the kinetics of the reaction which takes place in the liquid phase is required.

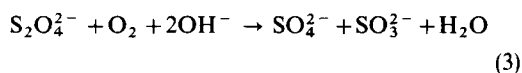
In an earlier work (Camacho *et al.*, 1992) using a gas–liquid stirred tank with a known flat interfacial surface, it was found in the ranges

$$\begin{aligned} 0.005 \text{ M} \leq [\text{S}_2\text{O}_4^{2-}] \leq 0.20 \text{ M} \\ 20,260 \text{ N/m}^2 \leq \text{PO}_2 \leq 101,300 \text{ N/m}^2 \\ 12.0 \leq \text{pH} \leq 13.7 \\ 293 \text{ K} \leq T \leq 318 \text{ K} \end{aligned} \quad (1)$$

that the reaction was of zero order with respect to oxygen and 1.5 for dithionite while the apparent kinetic constant was given, as a function of temperature, by the expression:

$$k = 3.22 \times 10^5 \exp(-4250/T), \text{ mol}^{-0.5} \text{ m}^{1.5} \text{ s}^{-1}. \quad (2)$$

In the experiments achieved in the aforementioned investigation, the pH was not kept constant but the initial concentrations of NaOH were always such that, taking into account the consumption of base due to the reaction



the pH value never fell below 12. In these conditions changes in the initial concentration of NaOH did not have any influence on the kinetics of the reaction.

Recently, using a gas–lift bubble column, Shaikh and Zaidi (1993) interpreted their results taking the order in respect to the dithionite to be 1 when the concentration was lower than 0.1 M and 2 when the concentration was higher. They also found that the absorption rate decreased as the pH of the solution increased, although their results from the analysis of this influence had an appreciable dispersion which prevented them from quantifying this effect. These authors studied the range of dithionite concentrations from 0.01 to 0.6 M and the range of pH between 8.5 and 13.7. In agreement with the experimental technique indicated, in each experiment a solution at the desired sodium dithionite concentration was prepared, the pH was adjusted with NaOH to the selected value and the absorption rate was measured by means of the fall in the gas flow through the contactor.

In the present paper, the results obtained from studies on pH influence on sodium dithionite oxidation with molecular oxygen in the alkaline range (pH ≥ 8) are shown in order to explain the divergences between both the aforementioned works.

### EXPERIMENTAL TECHNIQUE

The experiments were carried out in a gas–liquid stirred tank with a known flat interfacial surface (*A*<sub>i</sub> = 4.44 × 10<sup>−3</sup> m<sup>2</sup>), i.e. in the absence of bubbling in the liquid phase. The contactor was cylindrical, with an internal diameter of 7.5 × 10<sup>−2</sup> m, a capacity of 2.5 × 10<sup>−4</sup> m<sup>3</sup> and a speed-regulated mechanical agitator. It incorporated a thermostat to control the temperature and a combined electrode to measure the pH.

<sup>†</sup> Author to whom correspondence should be addressed.

All the kinetics experiments were performed under the same conditions of  $2.0 \times 10^{-4} \text{ m}^3$  liquid phase stirred at 250 rpm.

The gas flow from the cylinders was measured by means of a calibrated rotameter. The bottle was equipped with a needle valve for precision regulation of the flow ( $8.33 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ ). The gaseous phase approached saturation conditions by forcing the mixture through a porous-plate bubbler containing the same solution as the reactor in the thermostatic bath.

In order to perform the experiments with pure oxygen as the gas phase, the medium, an NaOH solution at the desired concentration, was saturated with nitrogen, after which a known quantity of solid sodium dithionite was added and allowed to dissolve completely. Samples were taken to determine the initial concentration. The oxygen was then allowed to circulate. The nitrogen dissolved in the initial liquid phase is completely displaced by oxygen. The dissolved oxygen concentration was measured using a polarographic  $\text{pO}_2$  electrode.

The absorption rate was measured by the change in composition of the liquid phase which was analysed through iodometric evaluation for the sum of dithionite and sulphite and by the quantity of alkali added to keep the pH constant at the desired value. Five experiments (pHs 11, 10, 9 and 8—in duplicate—respectively) were performed at 298 K, where the kinetic constant, calculated with eq. (2), is  $0.204 \text{ mol}^{-0.5} \text{ m}^{1.5} \text{ s}^{-1}$ .

Since the experimental equipment in contact with the liquid phase is made entirely of glass, the dithionite reaction was faster than the sulphite reaction and the dissolved oxygen concentration was zero throughout this process. Sulphite oxidation produced by the overall reaction does not occur at any appreciable rate.

The vapour pressure in the liquid phase was considered as corresponding to a NaOH solution at the same  $\text{Na}^+$  concentration as in the liquid phase (Perry and Chilton, 1984).

The constant of Henry's Law for the solubility of oxygen in water,  $H_0$ , was determined at the experimental temperature using the Hitcham expression, and corrected by the saline effect of the electrolytes present through the generalization of Sechenov's empirical equation

$$\log \left( \frac{H_d}{H_0} \right) = \sum_i h_i I_i \quad (4)$$

where  $I_i$  is the ionic strength for the salt  $i$  and  $h_i$  is the parameter for the corresponding saline effect for this salt (Schumpe, 1985). The values for  $h_i$  used for dithionite, sulphite and sulphate were provided by Hikita *et al.* (1978).

To estimate the diffusivity of oxygen in water,  $D_{\text{O}_2}$ , the Stokes-Einstein equation was used together with data compiled by Himmelblau (1964), Vivian and King (1964) and de Waal and Okeson (1966).

$$\frac{D_{\text{O}_2} \mu}{T} = 7.22 \times 10^{-15}, \quad \frac{N}{K} \quad (5)$$

To allow for the effect of any electrolytes present corrections were made using the equation proposed by Ho *et al.* (1986)

$$D_{\text{O}_2} = D_{\text{O}_2}(1 - f\sqrt{I}) \quad (6)$$

where values of  $f$ , i.e., the  $f$ -factor, depend on the nature of the salts in the electrolyte solution. The expression

$$f = A(M_S/\alpha_S)^n \quad (7)$$

should be used for the estimation of the  $f$ -factor, where  $A = 0.1187 (\text{l}^2/\text{g mol})^{1/4}$  and  $n = 1/4$ . Both were determined empirically by the authors.

In estimating the effective molecular weight,  $M_S$ , and the parameter  $\alpha_S$  of a mixed electrolyte solution, the algebraic combination rule using the mole fraction of each existing salt as the weighting parameter should be used, i.e.

$$M_S = \sum_i x_i M_i \quad (8)$$

and

$$\alpha_S = \sum_i x_i \alpha_i \quad (9)$$

where parameter  $\alpha_i$  is the ratio of the ionic strength to the molar concentration of the  $i$ -salt.

In determining the mass transfer coefficient the dynamic method was employed, since in the experimental conditions employed – without bubbling, low stirring rate and small specific interfacial area – this method is the most appropriate.

For this, pure nitrogen saturated with the liquid phase was allowed to circulate through the reactor, containing  $0.2 \times 10^{-3} \text{ m}^3$  of NaOH 0.2 M, and when the equilibrium was reached, the gaseous phase was instantly replaced by pure oxygen saturated with the liquid phase and the evolution in the dissolved oxygen concentration of the liquid phase was followed using a  $\text{pO}_2$  electrode. The  $k_1^0$  value obtained was  $6.5 \times 10^{-5} \text{ m/s}$ .

## DISCUSSION OF THE RESULTS

In agreement with eq. (3), the volumetric flow of oxygen, the rate of addition of base, together with the rates of disappearance of dithionite and the reducing power would have to be related by the equation

$$N_{\text{O}_2} a = \frac{1}{2} \frac{ds}{dt} = - \frac{d[\text{S}_2\text{O}_4^{2-}]}{dt} = - \frac{1}{4} \frac{dc}{dt} \quad (10)$$

where  $s$  represents the concentration of base added ( $\text{mol/m}^3$ ) and  $c$  the concentration of reducing power ( $\text{mol/m}^3$ ), since at work pHs, much greater than the  $\text{pK}_2$  of sulphurous and sulphuric acids, the sulphite and sulphate ions are completely dissociated.

In agreement with eq. (10), at each instant the relation between the concentration of reducing power and base added must be given by

$$c = c_0 - 2s \quad (11)$$

provided that during the process the oxidation of the

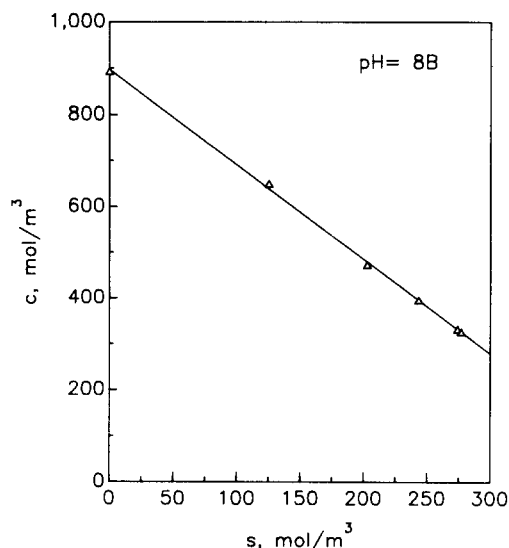


Fig. 1. Correlation between reducing power and base added.

sulphite does not take place. In order to prove this last equation, the reducing power is plotted against the base added in Fig. 1 for one of the experiments performed at pH 8, from which it can be seen that the experimental results fit the prediction of eq. (11) very well.

$$\text{Slope} = -2.060, \quad r^2 = 0.9992. \quad (12)$$

This result confirms that the process consisted entirely of the dithionite oxidation and that its disappearance rate may be followed by the diminution of reducing power or by the consumption of base.

Assuming that the reaction is zero order for molecular oxygen, as proposed in the majority of the papers published, the volumetric flow of oxygen in the fast reaction regime would be given by

$$N_{O_2}a = \sqrt{2D_{O_2}k[S_2O_4^{2-}]_b^m[O_2]_i}a. \quad (13)$$

In agreement with eq. (10), the volumetric flow of oxygen,  $N_{O_2}a$ , can be determined by differentiating the values of base added with respect to time, which was done using cubic splines. Thus eq. (13) can be realigned such that

$$\frac{(N_{O_2}a)^2}{2D_{O_2}[O_2]_i a^2} = k[S_2O_4^{2-}]_b^m \quad (14)$$

in order to take into account the changes in diffusivity and solubility of the oxygen caused by the reaction together with the addition of base to keep a constant pH. Figure 2 shows the experimental results obtained following eq. (14). It can be seen that, although there is an appreciable dispersion—due to the error implied in the differential calculus—one single straight-line fitted all the points, with no change of slope at the sodium dithionite concentration of 0.1M. However, the fact that all the results obtained from different experiments performed at several pHs coincide on one single straight line indicates that this variable has no influence on the kinetics of the reaction in the range

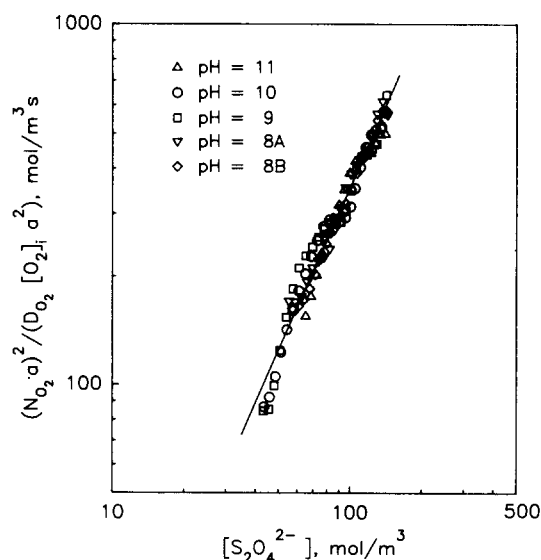


Fig. 2. Application of eq. (14).

Table 1

pH	<i>m</i>	<i>r</i> <sup>2</sup>
11	1.50	0.969
10	1.53	0.986
9	1.51	0.975
8A	1.48	0.990
8B	1.54	0.997

investigated. The results obtained by linear regression are shown in Table 1.

Assuming 1.5 order for dithionite, as the results indicate, it is possible to apply the integral method. In fact, combining eqs (10) and (13)

$$-\frac{d[S_2O_4^{2-}]}{dt} = \sqrt{2D_{O_2}k[S_2O_4^{2-}]^{1.5}[O_2]_i}a \quad (15)$$

which, separating variables and integrating, leads to

$$[S_2O_4^{2-}]^{0.25} = [S_2O_4^{2-}]_0^{0.25}$$

$$-0.25a(2k)^{0.5} \int_0^t \sqrt{D_{O_2}[O_2]_i} dt \quad (16)$$

where the integral on the right-hand side,  $I_t$ , allows the small changes in diffusivity and solubility of the oxygen, those caused by the increase of the ionic strength of the solution brought about by the reaction and addition of base, to be taken into account.

The results obtained using the way which was suggested by eq. (16) are represented in Fig. 3. A good fit to the equation is observed where the slopes are almost independent from the pH. By linear regression, the results indicated in Table 2 are obtained.

The values of the apparent kinetic constant calculated are represented against pH in Fig. 4, together with the value obtained in the previous work for the pH range 12–13.7, showing their great similarity, so

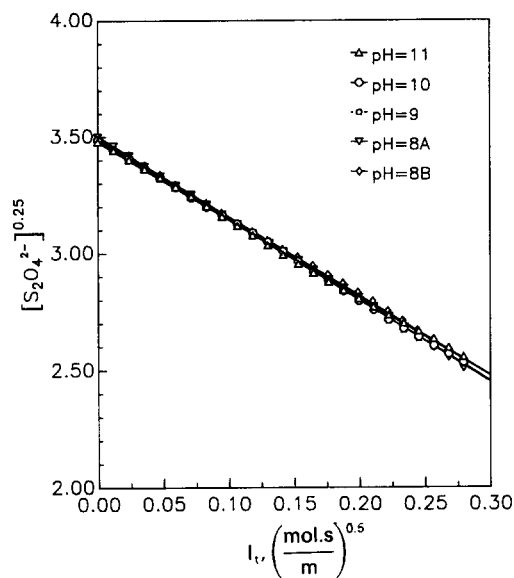


Fig. 3. Application of eq. (16).

Table 2

pH	$k$ (mol <sup>-0.5</sup> m <sup>1.5</sup> s <sup>-1</sup> )	$r^2$
11	0.194	0.9991
10	0.203	0.9997
9	0.209	0.9995
8A	0.211	0.9997
8B	0.194	0.9995

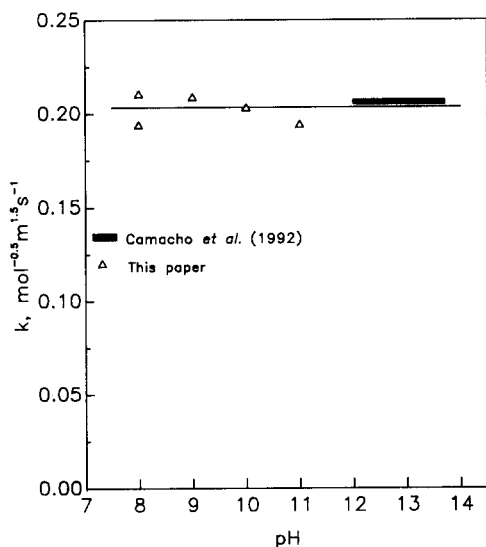


Fig. 4. Influence of the pH on the kinetic constant.

that at pHs higher than 8 the reaction kinetics seem not to be influenced by the value of this variable.

The results obtained verified the necessary conditions for obedience of the fast reaction regime

$$Ha = \sqrt{\frac{2D_{O_2}k[S_2O_4^{2-}]_b^{1.5}}{(k_1^0)^2[O_2]_i}} > 2 \quad (17)$$

$$Ha \ll \frac{[S_2O_4^{2-}]_b}{[O_2]_i} \quad (18)$$

In Table 3, the results which correspond to pH = 10 are shown, noting that Hatta's module is considerably higher than 2 in the 2 h range used, and also that condition (18) is observed.

Since Hatta's module rises by the power of 0.75 in respect to the dithionite concentration while the factor of chemical acceleration for instantaneous reaction,  $E_i$ , increases by the power of 1 in respect to the dithionite, there is only a lower limit to this concentration in the fast reaction regime, which is about 8 mol/m<sup>3</sup> in the contactor used in this investigation, in order to reach a Hatta value of 2.

On the contrary, in the contactor used by Shaikh and Zaidi (1993), the mass transfer coefficient is almost one order of magnitude higher:  $5.13 \times 10^{-4}$  m/s and, therefore, the corresponding limit value would be

$$[S_2O_4^{2-}] = (8) \left( \frac{5.13 \times 10^{-4}}{6.5 \times 10^{-5}} \right)^{1.5} \approx 125 \frac{\text{mol}}{\text{m}^3} \quad (19)$$

near to the value where these authors indicate that the change in the order takes place.

Moreover, if it is taken into account that when  $Ha < 2$ , the oxygen flow is given by

$$N_{O_2} = (\sqrt{1 + Ha^2}) k_l^0 [O_2]_i \quad (20)$$

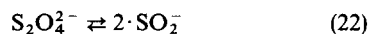
since 1 cannot be considered negligible compared to  $Ha^2$ , a minor dependence of  $N_{O_2}$  in respect to the dithionite concentration would be observed.

Regarding the order of 2 observed by the authors cited when the dithionite concentration was higher than 0.1 M, it is worth noting that the results upon which this assertion is based, Fig. 3 of their paper, suggest more an order of 1.5, since starting from this figure, an approximate order of 1.6 can be calculated graphically for the experiment at pH = 10.5 and 298 K, and 1.7 for the experiment at pH = 11.5 and 298 K.

In the opinion of the authors of the paper presented here, another factor involved in the change of order with respect to the dithionite concentration together with the influence of the pH noted by some researchers, is the dithionite disproportion, which occurs slowly at pH ≥ 8 and rapidly in acid solution (Greenwood and Earnshaw, 1984).



In this reference it is also indicated that electron-spin-resonance studies have shown the presence of the  $\cdot SO_2^-$  radical ion in sodium dithionite solution, suggesting the establishment of a monomer-dimer equilibrium



which is in agreement with one of the stages in the mechanism proposed by Camacho *et al.* (1992).

Table 3

$t$ (s)	$D_{O_2} \times 10^9$ (m <sup>2</sup> /s)	$[O_2]_i$ (mol/m <sup>3</sup> )	$Ha$	$[S_2O_4^{2-}]_b/[O_2]_i$
0	1.75	0.918	18.0	160.8
300	1.75	0.915	17.4	153.8
600	1.74	0.911	16.9	147.9
900	1.74	0.908	16.2	140.9
1200	1.73	0.904	15.7	135.0
1500	1.73	0.901	15.1	128.9
1800	1.72	0.898	14.5	122.7
2100	1.72	0.895	14.0	117.1
2400	1.71	0.893	13.5	112.3
2700	1.71	0.890	13.0	107.3
3000	1.71	0.888	12.6	102.3
3300	1.70	0.885	12.1	97.5
3600	1.70	0.883	11.6	92.7
3900	1.69	0.880	11.1	87.7
4200	1.69	0.878	10.7	82.9
4500	1.69	0.876	10.2	78.4
4800	1.69	0.874	9.8	74.2
5100	1.68	0.872	9.3	70.0
5400	1.68	0.870	9.0	66.4
5700	1.68	0.868	8.6	62.5
6000	1.67	0.867	8.2	59.1
6300	1.67	0.865	7.9	56.1
6600	1.67	0.864	7.6	53.1
6900	1.67	0.863	7.3	50.4
7200	1.67	0.862	7.0	47.7

#### Applicability of the process to interfacial area measurement

As it can be seen in Table 3, although diffusivity and solubility of the oxygen vary slightly with changes in ionic strength, these variations are partially compensated for in the value of Hatta's module, which for this system, at 298 K, would be given by

$$Ha = 2.8 \times 10^{-5} \frac{[S_2O_4^{2-}]^{0.75}}{k_i^0} \quad (23)$$

which allows determination of the minimum value of dithionite concentration,  $[S_2O_4^{2-}]_b$ , in order for it to take place within the fast reaction regime.

In the usual range of  $k_i^0$  in bubble stirred tanks, that is between  $5 \times 10^{-5}$  m/s and  $5 \times 10^{-4}$  m/s (Charpentier, 1981), this limit value will be between  $[S_2O_4^{2-}]_b = 6$  mol/m<sup>3</sup> and  $[S_2O_4^{2-}]_b = 120$  mol/m<sup>3</sup>, taking into account that  $Ha$  has to be higher than 2.

For the measurement of interfacial areas, it is necessary to study the dithionite oxidation process when its concentration is higher than this limit in which case the process rate is given by

$$-\frac{d[S_2O_4^{2-}]}{dt} = 2.4 \times 10^{-5} a [S_2O_4^{2-}]^{0.75} \quad (24)$$

using an average for the diffusivity and solubility of the oxygen, whose variations in the last expression are not compensated. Integrating eq. (24), leads to

$$[S_2O_4^{2-}]_b^{0.25} - [S_2O_4^{2-}]_i^{0.25} = 6 \times 10^{-6} at \quad (25)$$

therefore, when the specific interfacial area has a high value, of around 1000 m<sup>-1</sup>, and when the duration is

at least 300 s, the initial dithionite concentration might be around 600 mol/m<sup>3</sup>.

These calculations reveal the applicability of the process to interfacial area measurement, since the process can be followed automatically by the addition of base when the pH is controlled. They also indicate that the rate of the process can be an important restriction for very efficient contactors, those with high values of  $a$  and  $k_i^0$ .

It is evident that the process rate can be decreased using oxygen-nitrogen mixtures as gaseous phase, which implies the influence of the grade of mixture.

However, given that the reaction corresponding to the process is of zero order with respect to oxygen, the method is the least sensitive to the grade of mixture of the gaseous phase, which causes the greatest loss of precision in the application of chemical methods for determining interfacial areas using gaseous mixtures. Therefore, given the ionic strength of the solutions used, the method is applicable to non-coalescent systems (Oolman and Blanch, 1986).

#### NOTATION

$a$	specific interfacial area, m <sup>-1</sup>
$c$	equivalents of reducing power per m <sup>3</sup> of solution,
$D_{O_2}$	diffusivity of oxygen in the liquid phase, m <sup>2</sup> s <sup>-1</sup>
$Ha$	Hatta number
$I_i$	integral which corresponds to eq. (16)
$k$	kinetic constant, mol <sup>-0.5</sup> m <sup>1.5</sup> s <sup>-1</sup>
$k_i^0$	mass transfer coefficient, m s <sup>-1</sup>

$m$	reaction order in respect to B
$n$	reaction order in respect to A
$N_{O_2}$	flow across the interphase of oxygen, $\text{mol m}^{-2}$
$[O_2]_i$	oxygen concentration at the interphase
$r^2$	correlation coefficient
$s$	equivalents of base added per $\text{m}^3$ of solution
$[S_2O_4^{2-}]$	dithionite concentration, $\text{mol m}^{-3}$
$[S_2O_4^{2-}]_0$	initial dithionite concentration, $\text{mol m}^{-3}$
$[S_2O_4^{2-}]_b$	dithionite concentration in the liquid phase, $\text{mol m}^{-3}$
$[S_2O_4^{2-}]_i$	minimum dithionite concentration to be within fast reaction regime, $\text{mol m}^{-3}$
$t$	time, s
$\mu$	water viscosity, $\text{kg m}^{-1} \text{s}^{-1}$

## REFERENCES

- Camacho Rubio, F., Páez Dueñas, M<sup>a</sup>. P., Blázquez García, G. and Garrido Martín, J. M., 1992, Oxygen absorption in alkaline sodium dithionite solutions. *Chem. Engng Sci.* **47**, 4309–4314.
- Charpentier, J. C., 1981, Mass-transfer rates in gas–liquid absorbers and reactors. *Adv. Chem. Engng* **11**, 1–133.
- de Waal, K. J. A. and Okeson, J. C., 1966, Oxidation of aqueous sodium sulphite solutions. *Chem. Engng Sci.* **21**, 559–572.
- Greenwood, N. N. and Earnshaw, A., 1984, *Chemistry of the Elements*. Pergamon Press, Oxford.
- Hikita, H., Ishikawa, H., Sakamoto, N. and Esaka, N., 1978, Kinetics of absorption of oxygen in aqueous alkaline solutions of sodium dithionite. *Chem. Engng Sci.* **33**, 392–396.
- Himmelblau, D. M., 1964, Diffusion of dissolved gases in liquids. *Chem. Rev.* **64**, 527–550.
- Ho, C. S., Ju, L.-K. and Ho, C.-T., 1986, Measuring Oxygen Diffusion Coefficients with Polarographic Oxygen Electrodes. II Fermentation Media. *Biotechnol. Bioengng* **28**, 1086–1092.
- Jhaveri, A. S. and Sharma, M. M., 1968, Effective interfacial area in a packed column. *Chem. Engng Sci.* **23**, 669–676.
- Joshi, J. B. and Sharma, M. M., 1977, Mass transfer and hydrodynamic characteristics of gas inducing type of agitated contactors. *Can. J. Chem. Engng* **55**, 683–695.
- Oolmam, T. O. and Blanch, H. W., 1986, Bubble coalescence in air-sparged bioreactor. *Biotechnol. Bioengng* **28**, 578–584.
- Perry, R. H. and Chilton, C. H., 1984, *Chemical Engineers' Handbook*, 6th Edition, McGraw-Hill, New York.
- Sahay, B. N. and Sharma, M. M., 1973, Absorption in packed bubble columns. *Chem. Engng Sci.* **28**, 2245–2255.
- Shaikh, A. A. and Zaidi, S. M., 1993, *J. Chem. Tech. Biotechnol.* **56**, 139–145.
- Schumpe, A., 1985, Gas solubilities in biomedica, in *Biotechnology*, Vol. 2 (Edited by Brauer H.), pp. 159–170. VCH, Weinheim.
- Vivian, J. E. and King, C. J., 1964, Diffusivities of Slightly Soluble Gases in Water. *A.I.Ch.E. J.* **10**, 220–221.