



HAL
open science

Effect of organic solvents on oxygen mass transfer in multiphase systems: Application to bioreactors in environmental protection

Eric Dumont, Yves Andres, Pierre Le Cloirec

► **To cite this version:**

Eric Dumont, Yves Andres, Pierre Le Cloirec. Effect of organic solvents on oxygen mass transfer in multiphase systems: Application to bioreactors in environmental protection. *Biochemical Engineering Journal*, 2006, 30 (3), pp.245-252. 10.1016/j.bej.2006.05.003 . hal-00878492

HAL Id: hal-00878492

<https://hal.science/hal-00878492v1>

Submitted on 1 Feb 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Effect of organic solvents on oxygen mass transfer in multiphase systems: Application to bioreactors in environmental protection

E. Dumont*, Y. Andrès, P. Le Cloirec

Ecole des Mines de Nantes, UMR CNRS 6144 GEPEA, 4 rue Alfred Kastler, BP 20722, 44307 Nantes Cedex 03, France

The absorption of oxygen in aqueous–organic solvent emulsions was studied in a laboratory-scale bubble reactor at a constant gas flow rate. The organic and the gas phases were dispersed in the continuous aqueous phase. Volumetric mass transfer coefficients ($k_L a$) of oxygen between air and water were measured experimentally using a dynamic method. It was assumed that the gas phase contacts preferentially the water phase. It was found that addition of silicone oils hinders oxygen mass transfer compared to air–water systems whereas the addition of decane, hexadecane and perfluorocarbon PFC40 has no significant influence. By and large, the results show that, for experimental conditions (organic liquid hold-up $\leq 10\%$ and solubility ratio ≤ 10), the $k_L a$ values of oxygen determined in binary air–water systems can be used for multiphase (gas–liquid–liquid) reactor design with applications in environmental protection (water and air treatment processes).

Keywords: Absorption; Mass transfer; Multiphase reactors; Silicone oil; Oxygen; Bioprocesses

1. Introduction

Recent developments in bioreactor design have attempted to address some of the limitations of existing bioreactors. However, further progress in innovative bioreactor design remains a high priority, particularly for: (i) environmental bioreactors and (ii) increases in oxygen transfer from the gas phase to the microorganisms. In both cases, the addition of an organic solvent to the aqueous phase can be used to improve the efficiency of the bioprocess [1,2].

The development of environmental bioreactors is important for waste gas purification and treatment because polluted air has become of growing environmental and health concern. Recent papers have demonstrated that biological techniques often offer a cost-effective and environmentally friendly alternative to conventional air pollutant control technologies, such as catalytic oxidation or incineration [3–6]. Studies carried out in our laboratory have demonstrated the ability of bioscrubbing to deodorize waste gases and remove volatile organic compounds (VOC) from an air stream [7]. However, conventional

bioscrubbers can only be used for compounds that are readily soluble in water. For waste gases containing hydrophobic compounds having low solubility in water, the efficiency of the biological treatment is limited by the poor mass transfer of the pollutant from the gas phase to the aqueous phase. To overcome this problem, a multiphase bioscrubber was developed using a mixture of a non-biodegradable organic solvent and water to enable the absorption of the hydrophobic pollutant in an absorber (gas–liquid–liquid contactor). The water–solvent emulsion, with the absorbed pollutants mainly in the organic phase, is then transported to a bioreactor in which microorganisms degrade the pollutant dissolved in the aqueous phase. The lower pollutant concentration in the aqueous phase resulting from this process is the driving force for pollutant diffusion from the organic to the aqueous phase (Fig. 1). Thus, complete biological regeneration of the liquid is possible [8]. Numerous applications for the biodegradation of toxic and poorly water-soluble compounds improved by organic liquids have been described by Déziel et al. [9]. In addition, it is assumed that the organic solvent would enhance the oxygen mass transfer from the gas phase to the microorganisms in order to improve the degradation of the pollutant. Such a potential increase in the oxygen mass transfer due to the presence of organic solvent is also taken into account for the development of oxygen-limited bioreactors, as in the case of the microbial fermentation

* Corresponding author. Tel.: +33 2 51 85 82 66; fax: +33 2 51 85 82 99.

E-mail addresses: eric.dumont@emn.fr (E. Dumont), yves.andres@emn.fr (Y. Andrès), pierre.le-cloirec@emn.fr (P. Le Cloirec).

Nomenclature

a	interfacial area (m^{-1})
C_{gas}	oxygen concentration in air (mol m^{-3})
C_{org}	oxygen concentration in organic solvent (mol m^{-3})
C_{water}	oxygen concentration in water (mol m^{-3})
C_{water}^*	equilibrium concentration of oxygen between water and gas phase (mol m^{-3})
D	diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
H	Henry constant ($\text{Pa m}^3 \text{mol}^{-1}$)
k_L	mass transfer coefficient (m s^{-1})
$k_L a$	volumetric mass transfer coefficient (s^{-1})
m_R	solubility ratio
p_{oxygen}	partial pressure of oxygen in the gas phase (Pa)
P	total pressure of the gas phase (Pa)
Q_G	gas flow rate ($\text{m}^3 \text{s}^{-1}$)
R	universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
S	spreading coefficient (N m^{-1})
T	temperature (K)
u_G	gas velocity (m s^{-1})
V_G	volume of the gas phase (m^3)
V_L	volume of the liquid phase (m^3)
y_{oxygen}	oxygen mole fraction

Greek letters

ε	energy dissipation (W kg^{-1})
μ	dynamic viscosity (Pa s)
ρ	density (kg m^{-3})
σ	surface tension (N m^{-1})
ϕ	dispersed liquid phase hold-up

of products of commercial interest. Organic solvents would act as surface-active agents to lower the surface tension of water and increase the gaseous specific interfacial area. However, to date, the transfer mechanism of oxygen is not well

understood and it is not possible to propose a unified theory to describe satisfactorily the effect of the presence of organic solvent on the enhancement of the mass transfer of oxygen [10].

As oxygen mass transfer has a strong influence on bioprocess efficiency, we carried out experiments with a view to measuring, by a dynamic method, the volumetric mass transfer coefficient ($k_L a$) of oxygen in emulsions of water–organic solvent for the main organic liquids used in bioprocesses, i.e. dodecane, hexadecane, perfluorocarbons and silicone oils. Table 1 presents examples of organic solvents used in biological waste air treatment or to improve microbial production or fermentation. Experiments were carried out in a bubble column with the organic and gas phases dispersed in the continuous aqueous phase. This multiphase system represents the most unfavourable one for oxygen mass transfer because it is assumed that there is no contact between the gas phase and the organic phase.

2. Materials and methods

2.1. Chemicals

Dodecane and hexadecane were obtained from the Sigma–Aldrich Company. Perfluorocarbon PFC40 Fluorinert (primarily compounds with 12 carbons) was purchased from the 3M Company and silicone oils (Rhodorsil® fluids 47V5 and 47V10, dimethylpolysiloxane) were purchased from the Rhodia Company. The physical properties of these chemical products are summarized in Table 2. Spreading coefficients were obtained from Hassan and Robinson [47] for dodecane and hexadecane, from MacMillan and Wang [48] for PFC40, and from Basheva et al. [49] for silicone oil 47V5. Solubility ratios m_R (i.e. solubility of oxygen in organic liquid divided by solubility of oxygen in water) were obtained from Vadekar [50] for dodecane and hexadecane, from van Sonsbeek et al. [51] for PFC40, and from Dumont et al. [52] for silicone oils.

2.2. Equipment

A dynamic method, extensively described in [53], was used to determine the volumetric mass transfer coefficients of oxygen during absorption. In this method, a known gas volume, initially loaded with 20.9% oxygen, was continuously flowed via a circulating loop through the deoxygenated liquid system. The operation was batch wise with respect to the liquid system and the decrease in oxygen concentration in the gas phase was measured versus time. A schematic overview of the experimental set up is given in Fig. 2. The reactor used has an 11.5 L total volume (height 0.33 m, diameter 0.21 m). In the experiments, air was supplied from a compressor and sparged through an elliptical distributor (75 mm × 150 mm) with 50 holes (1 mm diameter). The superficial velocity of gas (u_G) was 0.01 m s^{-1} (gas flow rate $Q_G = 3.3 \times 10^{-4} \text{ m}^3 \text{ s}^{-1}$). All experiments were carried out, as presented in [53], at a constant temperature of 20°C maintained by the jacket. The total volumes of gas and liquid were 2 and 10 L, respectively.

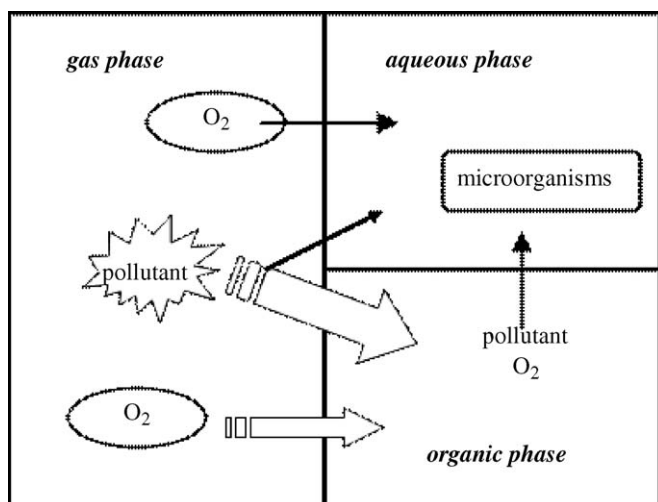


Fig. 1. Schematic representation of possible mass transfers in a multiphase gas–aqueous–organic phase system.

Table 1

Examples of organic solvents used to improve bioprocess efficiency (waste air treatment and fermentation)

Authors	Pollutant or fermentation	Microorganisms
Organic solvent: dodecane		
Daugulis and Janikowski [11]	Naphthalene; phenanthrene	<i>Sphingomonas aromaticivorans</i> B0695
Daugulis and McCracken [12]	Polyaromatic hydrocarbons	Two species of <i>Sphingomonas</i>
Galaction et al. [13]	B12 vitamin production	<i>Propionibacterium shermanii</i>
Janikowski et al. [14]	Polycyclic aromatic hydrocarbons	<i>S. aromaticivorans</i>
Jia et al. [15]	Yeast fermentation	<i>Saccharomyces cerevisiae</i> AY-12
Jianlong [16]	Citric acid production	<i>Aspergillus niger</i>
Lai et al. [17]	Lovastatin production	<i>Aspergillus terreus</i>
Organic solvent: hexadecane		
Brink and Tramper [18]	Oxygen; propene	<i>Mycobacterium</i> E3
Daugulis and Boudreau [19]	Toluene	<i>Alcaligenes xylosoxidans</i> Y234
Davidson and Daugulis [20,21]	(a) Toluene, benzene (b) Benzene	<i>A. xylosoxidans</i> Y234
Giridhar and Srivastava [22]	L-Sorbose fermentation	<i>Acetobacter suboxydans</i>
Ho et al. [23]	Penicillin fermentations	<i>Penicillium chrysogenum</i>
Yeom et al. [24]	Benzene	<i>A. xylosoxidans</i> Y234
Organic solvent: perfluorocarbon PFC40		
Cesario et al. [25,26]	Ethane	<i>Mycobacterium parafortuitum</i>
Cesario et al. [27,28]	Toluene	
Cesario et al. [29]	Toluene	<i>Pseudomonas putida</i> GJ40
Elibol and Mavituna [30]	Antibiotic production	<i>Streptomyces coelicolor</i>
Menge et al. [31]	Alkaloid production	<i>Claviceps purpurea</i>
Takeshi et al. [32]	Fermentation of insect cells (<i>Spodoptera frugiperda</i>)	
Organic solvent: silicone oil		
Aldric et al. [33]	Isopropyl-benzene	<i>Rhodococcus erythropolis</i> T902
Ascon-Cabrera and Lebeault [34]	Ethyl butyrate	<i>Candida</i> sp. CF3
Bouchez et al. [35]	Phenanthrene	<i>Pseudomonas</i> sp.
Bouchez et al. [36]	Polycyclic aromatic hydrocarbons	<i>Pseudomonas</i> sp., <i>Pseudomonas stutzeri</i> , <i>Rhodococcus</i> sp.
Budwill and Coleman [37]	Hexane	<i>Microbial consortium</i>
Cesario et al. [38]	2-Butanol; hexane; toluene; ethylmethylketone; butylacetate	
El Aalam et al. [39]	Styrene	<i>Pseudomonas aeruginosa</i>
Fazaelipoor and Shojaosadati [40]	Hexane (80%) + hydrocarbons	
Gardin et al. [41]	Xylene; butyl acetate	Mixed culture
Hekmat and Vortmeyer [42]	Methyl ethyl benzene Diethyl benzene	Mixed culture
Lebeault [43]	Toluene	Mixed culture
Lebeault et al. [44]	Styrene	<i>P. aeruginosa</i> , <i>P. putida</i>
Osswald et al. [45]	Styrene	<i>Consortium</i> of slightly-halophile marine bacteria
Vannek et al. [46]	Polycyclic aromatic hydrocarbons	

3. $k_L a$ calculation

3.1. Assumptions

The dynamic method for $k_L a$ measurement in air–water–oil systems is based on the gas phase mass balance and on the off-gas

analysis technique, which has been proved a relevant measurement method [54–56]. $k_L a$ measurement is supported by some assumptions:

1. In the reactor, the ideal gas law is applicable to calculate the number of moles of oxygen absorbed by the liquid. The

Table 2

Physical properties of the organic phase used ($T=25^\circ\text{C}$)

	Viscosity (mPa s)	Density (kg m ⁻³)	Spreading coefficient (mN m ⁻¹)	Solubility ratio m_R
Dodecane	1.3	740	-2.7	6
Hexadecane	3.0	773	-9.3	5
Perfluorocarbon PFC40	3.4	1850	+4.0	12
Silicone oil 47V5	5.0	910	+6.6	7
Silicone oil 47V10	10.0	930	-	7

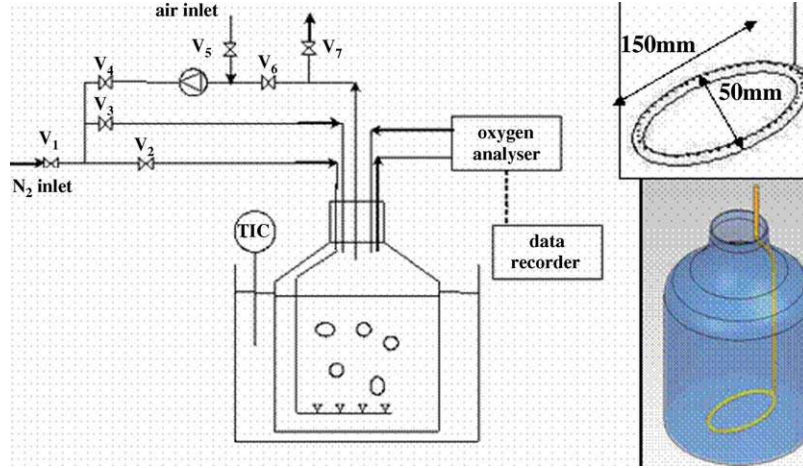


Fig. 2. Schematic overview of the experimental set up used to determine $k_L a$ (TIC: temperature indicator control).

operating conditions justify such an assumption, since temperature and pressure are low.

2. The resistance of oxygen transfer in the gas phase is neglected, which is nearly always permitted [57]. Thus, the overall mass transfer coefficient is considered as the liquid phase mass transfer coefficient $k_L a$.
3. The liquid phase can be reasonably estimated as perfectly mixed. This may be assumed considering the convective recirculation and turbulence caused by the rising gas bubbles leading to a much shorter mixing time than the characteristic mass transfer time, $1/k_L a$.
4. The gas phase is considered as plug flow in the closed flowing circuit as in the oxygen analyser circuit.
5. The presence of an organic solvent in the emulsion does not change the Henry constant for oxygen in water.
6. There is no contact between the gas and the organic liquid phase.
7. As liquid–liquid mass transfer is very fast compared to gas–liquid mass transfer, a liquid–liquid equilibrium in terms of oxygen concentration can be assumed during oxygen absorption.
8. The response time for the paramagnetic oxygen analyser is less than 5 s, which is less than the mass transfer response time of the system: $1/k_L a$.

3.2. Derivation of $k_L a$

In the system including three phases, the total change in concentration of oxygen in air C_{gas} is due to the amount of oxygen absorbed in the water phase (continuous liquid phase) and to the amount of oxygen absorbed in the organic phase (dispersed liquid phase):

$$-V_G \frac{dC_{\text{gas}}}{dt} = V_L(1 - \phi) \frac{dC_{\text{water}}}{dt} + V_L \phi \frac{dC_{\text{org}}}{dt} \quad (1)$$

V_L is the total volume of the liquid phase and V_G is the total volume of the gas phase. C_{water} and C_{org} are the concentrations of oxygen in water and organic phases, respectively. ϕ is the

dispersed liquid phase hold-up (volume of organic liquid phase as a fraction of total liquid phase volume).

As the water phase and the organic phase are assumed to be in equilibrium at any time (assumption 7):

$$C_{\text{org}} = m_R C_{\text{water}} \quad (2)$$

m_R is the solubility ratio defined as the ratio of the solubility of oxygen in the organic phase to that in water. Oxygen dissolves much better in organic solvents than in water (Table 2).

Eqs. (1) and (2) lead to:

$$-\frac{dC_{\text{gas}}}{dt} = \frac{V_L}{V_G} (1 + \phi(m_R - 1)) \frac{dC_{\text{water}}}{dt} \quad (3)$$

The oxygen concentration in the constant volume of gas is obtained from mass balance:

$$C_{\text{gas}} = \frac{P}{RT} y_{\text{oxygen}} \quad (4)$$

where y_{oxygen} is the mole fraction of oxygen in the gas phase and P is the total pressure in the gas phase considered constant during the experiment. After differentiating with respect to time t , Eq. (5) is obtained from Eq. (4):

$$\frac{dC_{\text{gas}}}{dt} = \frac{P}{RT} \frac{dy_{\text{oxygen}}}{dt} \quad (5)$$

Combining Eqs. (5) and (3) gives, after integrating between $t=0$ ($C_{\text{water}}=0$ and $y_{\text{oxygen}}=y_{\text{oxygen}(t=0)}$) and t :

$$C_{\text{water}} = -\frac{V_G}{V_L} \frac{1}{1 + \phi(m_R - 1)} \frac{P}{RT} (y_{\text{oxygen}(t)} - y_{\text{oxygen}(t=0)}) \quad (6)$$

According to assumptions 3 (liquid phase perfectly mixed) and 6 (no contact between the gas and the organic phase), the mass transfer rate in the gas liquid system is given by:

$$-V_G \frac{P}{RT} \frac{dy_{\text{oxygen}}}{dt} = k_L a V_L (C_{\text{water}}^* - C_{\text{water}}) \quad (7)$$

$k_L a$ is based on the total volume of the liquid (aqueous and organic phases) instead of the aqueous volume to avoid an appar-

ent increase in value solely due to a decrease in the aqueous phase volume. C_{water}^* is the equilibrium concentration between water and the absorbed gas phase. C_{water}^* is defined according to Eq. (8), where p_{oxygen} is the partial pressure of oxygen in the gas phase and H is the Henry constant for oxygen in water:

$$C_{\text{water}}^* = \frac{p_{\text{oxygen}}}{H} \quad (8)$$

Dividing by the total pressure P , Eq. (8) becomes:

$$C_{\text{water}}^* = \frac{P}{H} \frac{p_{\text{oxygen}}}{P} = \frac{P}{H} y_{\text{oxygen}} \quad (9)$$

Introducing the expression of C_{water} and C_{water}^* in Eq. (7) gives:

$$\begin{aligned} & \frac{V_G}{V_L} \frac{P}{RT} \frac{dy_{\text{oxygen}}}{dt} \\ &= k_L a \left[\frac{P}{H} y_{\text{oxygen}} + \frac{V_G}{V_L} \frac{1}{1 + \phi(m_R - 1)} \right. \\ & \quad \left. \times \frac{P}{RT} (y_{\text{oxygen}(t)} - y_{\text{oxygen}(t=0)}) \right] \quad (10) \end{aligned}$$

whose integration between $t=0$ and t gives:

$$\begin{aligned} & \left[\frac{1}{\alpha + (1/(1 + \phi(m_R - 1)))} \right] \\ & \times \ln \left\{ \frac{\alpha y_{\text{oxygen}(t=0)}}{[\alpha + (1/(1 + \phi(m_R - 1)))] y_{\text{oxygen}(t)} - y_{\text{oxygen}(t=0)}/1 + \phi(m_R - 1)} \right\} = k_L a t \quad (11) \end{aligned}$$

with $\alpha = V_L RT / V_G H$. By plotting the left-hand side of Eq. (11) versus time, we obtained a straight line whose slope gives the volumetric mass transfer coefficient $k_L a$ for the aqueous phase in the presence of organic phase. Introducing $\phi=0$ in Eq. (11) allows the determination of $k_L a$ in a binary air–water system.

4. Experimental results and discussion

Binary air–water system: 39 measurements were carried out. For each experiment, the decrease in the mole fraction of oxygen (y_{oxygen}) in the gas phase versus time was recorded. The determination of $k_L a$ from experimental data was then obtained by using Eq. (11). Typical representations of $k_L a$ determinations have previously been published [52,53]. For our apparatus and the hydrodynamic conditions ($u_G = 0.01 \text{ m s}^{-1}$), $k_L a$ values ranged from 0.0132 to 0.0178 s^{-1} (mean value $k_L a^{\text{ref.}}$: 0.0156 s^{-1} ; standard deviation 15%; grey zone in Fig. 3).

Air–water–organic phase: experiments were carried out in triplicate using several emulsion compositions, varying from 0 to 4% for PFC40 and from 0 to 10% for silicone oils, dodecane and hexadecane. Fig. 3 presents the $k_L a$ results for all organic solvents (maximum deviation: $\pm 15\%$) compared with those obtained for an air–water system without an organic phase in the same hydrodynamic conditions. Addition of silicone oils hinders the volumetric mass transfer coefficient of oxygen compared to air–water systems. The effects are greater for the most viscous silicone oil (47V10). Decreases in $k_L a$ of up to 25% are

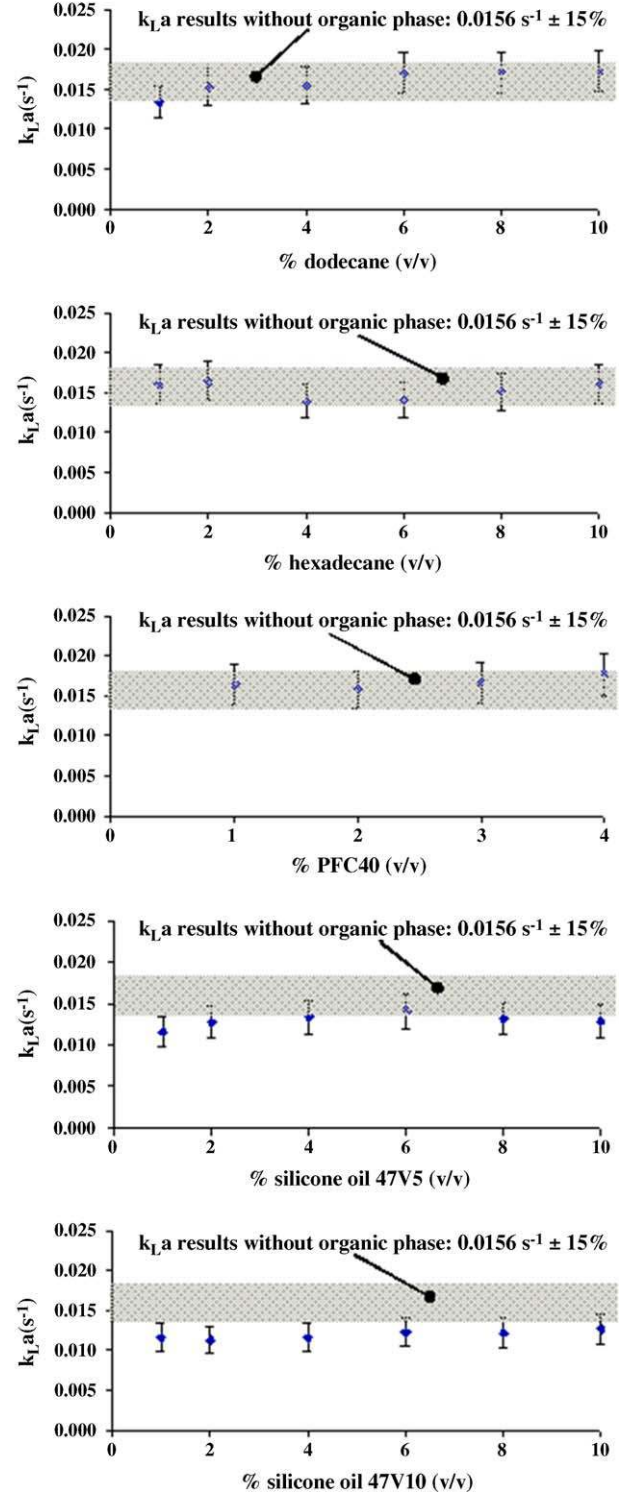


Fig. 3. Experimental $k_L a$ values for oxygen absorption in emulsions of aqueous–organic phase as a function of the organic phase volume fraction ($u_G = 0.01 \text{ m s}^{-1}$).

noted. Conversely, taking into account the accuracy of measurement, Fig. 3 shows that organic phase addition has no significant influence on $k_L a$ results in the cases of dodecane, hexadecane and perfluorocarbon PFC40. In the latter case, the high density (1850 kg m^{-3}) of the organic phase leads to a specific behaviour

of the liquid phase. Whereas bubbling leads to oil droplet formation in the continuous water phase for organic phases lighter than water, PFC40 settles at the bottom of the reactor for all the amounts added. In this case, the perfluorocarbon remains under the gas distributor and it is not possible to disturb it sufficiently to disperse droplets in the bulk of the water. However, the interface between the organic phase and water is continuously moved by the recirculating flow of water in the reactor. Due to the absence of droplets and the non-miscibility of PFC40 in water, it could be assumed that the organic phase does not influence the hydrodynamic conditions and the interfacial area, which is consistent with the experimental $k_L a$ measurements. MacMillan and Wang [48], measuring the air bubble size distribution by a photographic method, showed that the interfacial area in PFC40 dispersions was independent of PFC loading from 0 to 15% (v/v). Similar trend was reported by Yamamoto et al. [1] for PFC loading up to 60% (v/v).

Considering the influence of organic phase addition on $k_L a$ only, contrasting results have been reported in the literature. In a review devoted to gas absorption in oil-in-water systems, Dumont and Delmas [10] reported that the $k_L a$ value can decrease, remain unaffected or increase upon addition of the organic phase. For instance, Hassan and Robinson [47] found, for the same experimental conditions, that hexadecane addition increases $k_L a$ whereas dodecane addition decreases $k_L a$. Unfortunately, these authors were not able to explain these opposing results. To date, a satisfactory assessment of the influence of the addition of small amounts of organic phase on the mass transfer of oxygen remains difficult. Nonetheless, a recent model has been proposed [58]. This model takes both shuttle effects and hydrodynamic effects into account to calculate the enhancement factor due to the presence of the organic liquid droplets. The general expression of this model is:

$$\frac{(k_L a)_\phi}{(k_L a)_{\phi=0}} = \left(\frac{D_\phi}{D_{\phi=0}} \right)^{1/2} \left(\frac{\mu_{\phi=0} \rho_\phi \varepsilon_\phi}{\mu_\phi \rho_{\phi=0} \varepsilon_{\phi=0}} \right)^{1/4} \quad (12)$$

The first term of the right-hand side expression represents the influence of the shuttle effect on the enhancement; the second represents the hydrodynamic effect. D is the diffusion coefficient of oxygen, μ the dynamic viscosity of the emulsion, ρ the density of the emulsion and ε corresponds to the energy dissipation rate of the system. $\phi = 0$ and ϕ correspond to the binary air–water system and multiphase system, respectively. An assessment of the influence of the shuttle effect is difficult to calculate. For our system ($\phi \leq 0.1$ and $m_R < 10$) and, according to Fig. 4 from [58], the shuttle effect should range from 1 to 1.2. For the hydrodynamic effect, the energy dissipation rate is assumed unchanged between each experiment. Thus, the change in $k_L a$ is due only to the change in the density and the dynamic viscosity of the emulsion with the addition of oil. Calculations of μ_ϕ and ρ_ϕ are detailed in [58]. According to Eq. (12) and the data gathered in Table 2, it appears that the hydrodynamic effect ranges from 1 to 0.95 when ϕ varies from 0 to 10%. Finally, the modelled $k_L a$ values calculated for all organic phases ($0 \leq \phi \leq 0.1$), and taking into account both shuttle and hydrodynamic effects, are within the maximum deviation of the experimental results.

As demonstrated experimentally, the addition of an organic phase has no significant positive influence on the volumetric mass transfer coefficient of oxygen for our experimental conditions. The results obtained could be explained by the interfacial properties of the emulsions, particularly by the spreading coefficient defined as:

$$S = \sigma_{AW} - \sigma_{OW} - \sigma_{OA} \quad (13)$$

where σ are interfacial tensions and the subscripts AW, OW and OA refer to air–water, oil–water and oil–air interfaces, respectively. A positive value of S is considered to correspond to easy spreading of the oil droplet on gas bubbles. For dodecane and hexadecane, S is negative (Table 2), which implies that the organic solvent remains as discrete droplets and does not contact the gas bubbles. In both cases, the transfer is not affected by the presence of organic droplets and $k_L a$ remains roughly constant. For silicone oils, S is “initially” positive (Table 2; S is calculated with the values of pure component surface tension), which implies that these organic phases should be able to spread on the gas–aqueous surface. However, when the aqueous and organic phases are mutually saturated, Basheva et al. [49,59] have demonstrated that S becomes negative at equilibrium ($S = -0.8 \text{ mN m}^{-1}$ for silicone oil whose viscosity is 5 mPa s), which ultimately implies that silicone oil remains as discrete droplets. Morao et al. [60], who found similar changes in $k_L a$ with silicone oil addition, discussed the influence of silicone oil on both k_L and a . According to these authors, silicone oil, acting as an antifoam agent, has two opposing effects on the interfacial area a . On the one hand, silicone oil lowers the surface tension between gas and liquid, thus decreasing the bubble diameter and consequently increasing a . On the other hand, silicone oil tends to promote coalescence, thus decreasing a . Morao et al. [60] and Kawase and Moo-Young [61] suggested that these opposing effects more or less cancel each other out, and hence the most important effect is on the film coefficient k_L . According to [60], the variation in the relative $k_L a$ measurements (decreasing then increasing with oil addition, Fig. 3) can be explained by three effects; as oil concentration increases, (i) bubble surface mobility decreases, (ii) coalescence is enhanced and (iii) surface tension decreases. The first two effects, which depress $k_L a$, may however reach a limit, namely when all contacting bubbles coalesce and mobility is suppressed. Meanwhile, surface tension keeps decreasing, reducing bubble size, and hence $k_L a$ starts to rise. According to this explanation, there is a critical concentration at which the gas–liquid mass transfer is minimal.

While contradictory results exist about the actual mechanisms of mass transfer in gas–water–organic systems [10], it seems that the relationship between the mass transfer coefficient $k_L a$ and the physical–chemical properties of the emulsion are not sufficiently taken into account and should be reconsidered.

In summary, it appears that the use of an organic phase is a good strategy for enhancing the productivity of cultures by microorganisms or allowing the biodegradation of gaseous hydrophobic pollutants, whatever the bioreactor design. Firstly, the organic phase acts as an oxygen reservoir, increasing the oxygen driving force between the air and the water–oil emul-

sion and allowing the enhancement of the oxygen uptake rate from the air to the microorganisms. Several positive results have been reported from the literature for all the organic phases used: hexadecane [2,22,23]; dodecane [15–17]; perfluorocarbons [1,2,15,30,31]; concerning the use of silicone oils, the observed decrease in $k_{L}a$ with oil addition can be compensated by the increase in the driving force according to the amounts of oil added. Dumont et al. [53] have shown that addition of more than 5% silicone oil is beneficial to increasing the oxygen uptake rate. Secondly, the organic liquid acts both as a pollutant reservoir and an oxygen reservoir to enhance the degradation of gaseous pollutants with low solubility in water.

5. Conclusion

Volumetric mass transfer coefficients ($k_{L}a$) of oxygen between air and water in different gas–aqueous–organic phase systems have been measured experimentally using a dynamic method. Experiments were carried out in the most unfavourable multiphase system for oxygen mass transfer (organic phase dispersed in the aqueous phase). Addition of silicone oils hinders oxygen mass transfer compared to air–water systems whereas the addition of decane, hexadecane and perfluorocarbon PFC40 has no significant influence. The negative influence of silicone oil addition on the oxygen uptake rate is nonetheless reduced as soon as the amount added is more than 5%. By and large, the addition of a non-biodegradable organic solvent, acting as an oxygen reservoir and/or a substrate reservoir, improves the efficiency of bioprocesses. For our experimental conditions (organic liquid hold-up $\leq 10\%$ and solubility ratio ≤ 10), the results obtained show that the $k_{L}a$ values of oxygen determined in binary air–water systems can be used in multiphase (gas–liquid–liquid) reactor design.

References

- [1] S. Yamamoto, H. Honda, N. Shiragami, H. Unno, Analysis of oxygen transfer enhancement by oxygen carriers in the autotrophic cultivation of *Alcaligenes eutrophus* under lower oxygen partial pressure, *J. Chem. Eng. Jpn.* 27 (1994) 449–454.
- [2] S. Yamamoto, H. Kuriharan, T. Furuya, X.-H. Xing, H. Honda, N. Shiragami, H. Unno, Selection criteria of oxygen carriers utilizable for autotrophic growth improvement of *Alcaligenes eutrophus* under lowered oxygen partial pressure, *J. Chem. Eng. Jpn.* 28 (1995) 218–220.
- [3] M.A. Deshusses, Biological waste air treatment in biofilter, *Environ. Biotechnol.* 8 (1997) 335–339.
- [4] H.H.J. Cox, M.A. Deshusses, Biological waste air treatment in biotrickling filters, *Environ. Biotechnol.* 9 (1998) 256–262.
- [5] C. Kennes, F. Thalasso, Waste gas biotreatment technology, *J. Chem. Technol. Biotechnol.* 72 (1998) 303–319.
- [6] J.W. van Groenestijn, N.J.R. Kraakman, Recent developments in biological waste gas purification in Europe, *Chem. Eng. J.* 113 (2005) 85–91.
- [7] P. Humeau, P. Pr e, P. Le Cloirec, Optimization of bioscrubber performances: experimental and modeling approaches, *J. Environ. Eng.* 130 (2004) 314–321.
- [8] C. Kennes, M.C. Veiga, *Bioreactors for Waste Gas Treatment*, Kluwer Academic Publishers, 2001, pp. 148–151.
- [9] E. D eziel, Y. Comeau, R. Villemur, Two-liquid-phase bioreactors for enhanced degradation of hydrophobic/toxic compounds, *Biodegradation* 10 (1999) 219–233.
- [10] E. Dumont, H. Delmas, Mass transfer enhancement of gas absorption in oil-in-water systems: a review, *Chem. Eng. Process.* 42 (2003) 419–438.
- [11] A.J. Daugulis, T.B. Janikowski, Scale-up performance of a partitioning bioreactor for the degradation of polyaromatic hydrocarbons by *Sphingomonas aromaticivorans*, *Biotechnol. Lett.* 24 (2002) 591–594.
- [12] A.J. Daugulis, C.M. McCracken, Microbial degradation of high and low molecular weight polyaromatic hydrocarbons in a two-phase partitioning bioreactor by two strains of *Sphingomonas* sp., *Biotechnol. Lett.* 25 (2003) 1441–1444.
- [13] A.I. Galaction, D. Cascaval, M. Turnea, E. Folescu, Enhancement of oxygen mass transfer in stirred bioreactors using oxygen-vector, 2. *Propionibacterium shermanii* broths, *Bioprocess Biosyst. Eng.* 27 (2005) 263–271.
- [14] T.B. Janikowski, D. Velicogna, M. Punt, A.J. Daugulis, Use of a two-phase bioreactor for degrading polycyclic aromatic hydrocarbons by a *Sphingomonas* sp., *Appl. Microbiol. Biotechnol.* 59 (2002) 368–376.
- [15] S. Jia, M. Wang, P. Kahar, Y. Park, M. Okabe, Enhancement of yeast fermentation by addition of oxygen vectors in air-lift bioreactors, *J. Ferment. Bioeng.* 84 (1997) 176–178.
- [16] W. Jianlong, Enhancement of citric acid production by *Aspergillus niger* using *n*-dodecane as an oxygen-vector, *Process Biochem.* 35 (2000) 1079–1083.
- [17] L.S.T. Lai, T.H. Tsai, T.C. Wang, Application of oxygen vectors to *Aspergillus terreus* cultivation, *J. Biosci. Bioeng.* 94 (2002) 453–459.
- [18] L.E.S. Brink, J. Tramper, Facilitated mass transfer in a packed-bed immobilized-cell reactor by using an organic solvent as substrate reservoir, *J. Chem. Technol. Biotechnol.* 37 (1987) 21–44.
- [19] A.J. Daugulis, N.G. Boudreau, Removal and destruction of high concentrations of gaseous toluene in a two-phase partitioning bioreactor by *Alcaligenes xylooxidans*, *Biotechnol. Lett.* 25 (2003) 1421–1424.
- [20] C.T. Davidson, A.J. Daugulis, Addressing biofilter limitations: a two-phase partitioning bioreactor process for the treatment of benzene and toluene contaminated gas streams, *Biodegradation* 14 (2003) 415–421.
- [21] C.T. Davidson, A.J. Daugulis, The treatment of gaseous benzene by two-phase partitioning bioreactors: a high performance alternative to the use of biofilters, *Appl. Microbiol. Biotechnol.* 62 (2003) 297–301.
- [22] R. Giridhar, A.K. Srivastava, Productivity enhancement in L-sorbose fermentation using oxygen vector, *Enzyme Microb. Technol.* 27 (2000) 537–541.
- [23] C.S. Ho, L.K. Ju, J.R.F. Baddour, Enhancing penicillin fermentations by increased oxygen solubility through the addition of *n*-hexadecane, *Biotechnol. Bioeng.* 36 (1990) 1110–1118.
- [24] S.H. Yeom, M.C.F. Dalm, A.J. Daugulis, Treatment of high-concentration gaseous benzene streams using a novel bioreactor system, *Biotechnol. Lett.* 22 (2000) 1747–1751.
- [25] M.T. Ces ario, M. Turtoi, S.F.M. Sewalt, H.H. Beftink, J. Tramper, Enhancement of the gas-to-water ethane transfer coefficient by a dispersed water-immiscible solvent: effect of the cells, *Appl. Microbiol. Biotechnol.* 46 (1996) 497–502.
- [26] M.T. Ces ario, J.B. Brandsma, M.A. Boon, J. Tramper, H.H. Beftink, Ethene removal from gas by recycling a water-immiscible solvent through a packed absorber and a bioreactor, *J. Biotechnol.* 62 (1998) 105–118.
- [27] M.T. Ces ario, H.L. de Wit, J. Tramper, H.H. Beftink, New technique for $k_{L}a$ measurement between gas and water in aerated solvent-in-water dispersions, *Biotechnol. Tech.* 10 (1996) 195–198.
- [28] M.T. Ces ario, H.L. de Wit, J. Tramper, H.H. Beftink, Dispersed organic solvent to enhance the overall gas/water mass transfer coefficient of apolar compounds in the biological waste-gas treatment. Modeling and evaluation, *Biotechnol. Prog.* 13 (1997) 399–407.
- [29] M.T. Ces ario, W.A. Beverloo, J. Tramper, H.H. Beftink, Enhancement of gas–liquid mass transfer rate of apolar pollutants in the biological waste gas treatment by a dispersed organic solvent, *Enzyme Microb. Technol.* 21 (1997) 578–588.
- [30] M. Elibol, F. Mavituna, A remedy to oxygen limitation problem in antibiotic production: addition of perfluorocarbon, *Biochem. Eng. J.* 3 (1999) 1–7.

- [31] M. Menge, J. Mukherjee, T. Scheper, Application of oxygen vectors to *Claviceps purpurea* cultivation, *Appl. Microbiol. Biotechnol.* 55 (2001) 411–416.
- [32] G. Takeshi, M. Gaku, K. Ken-Ichi, A novel column fermentor having a wetted-wall of perfluorocarbon as an oxygen carrier, *Biochem. Eng. J.* 8 (2001) 165–169.
- [33] J.M. Aldric, J. Destain, P. Thonart, The two-phase reactor water/silicone oil: prospects in the off-gas treatment, in: Verstraete (Ed.), *European Symposium on Environmental Biotechnology, ESEB, 2004*, pp. 855–859.
- [34] M.A. Ascon-Cabrera, J.M. Lebeault, Cell hydrophobicity influencing the activity/stability of xenobiotic degrading microorganisms in a continuous biphasic aqueous–organic systems, *J. Ferment. Bioeng.* 80 (1995) 270–275.
- [35] M. Bouchez, D. Blanchet, J.P. Vandecasteele, Substrate availability in phenanthrene biodegradation: transfer mechanism and influence on metabolism, *Appl. Microbiol. Biotechnol.* 43 (1995) 952–960.
- [36] M. Bouchez, D. Blanchet, B. Besnainou, J.Y. Leveau, J.P. Vandecasteele, Kinetic studies of biodegradation of insoluble compounds by continuous determination of oxygen consumption, *J. Appl. Microbiol.* 82 (1997) 310–316.
- [37] K. Budwill, R.N. Coleman, Effect of silicone oil on biofiltration of *n*-hexane vapours, *Med. Fac. Landbouww. Univ. Gent.* 62 (4b) (1997) 1521–1527.
- [38] M.T. Cesário, H.H. Beertink, J. Tramper, Biological treatment of waste gases containing poorly-water-soluble pollutants, in: A.J. Dragt, J. van Ham (Eds.), *Biotechniques for Air Pollution Abatement and Odour Control Policies*, Elsevier Science Publishers B.V., 1992, pp. 135–140.
- [39] S. El Aalam, A. Pauss, J.M. Lebeault, High efficiency styrene biodegradation in a biphasic organic/water continuous reactor, *Appl. Microbiol. Biotechnol.* 39 (1993) 696–699.
- [40] M.H. Fazaelpoor, S.A. Shojaosadati, The effect of silicone oil on biofiltration of hydrophobic compounds, *Environ. Prog.* 21 (2002) 221–224.
- [41] H. Gardin, J.M. Lebeault, A. Pauss, Biodegradation of xylene and butyl acetate using an aqueous–silicon oil two-phase system, *Biodegradation* 10 (1999) 193–200.
- [42] D. Hekmat, D. Vortmeyer, Biodegradation of poorly water-soluble volatile aromatic compounds from waste air, *Chem. Eng. Technol.* 23 (2000) 315–318.
- [43] J.M. Lebeault, Biological purification of waste gases by fermentation in a multiphase bioreactor, *Med. Fac. Landbouww. Rijksuniv. Gent.* 55 (1990) 1424–1428.
- [44] J.M. Lebeault, M. Nonus, R. Djeribi, T. Dezenclous, Solubilisation and biodegradation of organic pollutants in biphasic organic systems, *VDI Berichte* 1241 (1996) 531–537.
- [45] P. Osswald, P. Baveye, J.C. Block, Bacterial influence on partitioning rate during the biodegradation of styrene in a biphasic aqueous–organic system, *Biodegradation* 7 (1996) 297–302.
- [46] P. Vanneck, M. Beekman, N. de Saeyer, S. D’Haene, W. Verstraete, Biodegradation of polycyclic aromatic hydrocarbons in a two-liquid-phase system, in: R.E. Hinchee, D.B. Anderson, R.E. Hoepfel (Eds.), *Bioremediation of Recalcitrant Organics*, vol. 7, Battelle Press, 1995, pp. 55–62.
- [47] I.T.M. Hassan, C.W. Robinson, Oxygen transfer in mechanically agitated aqueous systems containing dispersed hydrocarbon, *Biotechnol. Bioeng.* 19 (1977) 661–682.
- [48] J.D. MacMillan, D.I.C. Wang, Mechanisms of oxygen transfer enhancement during submerged cultivation in perfluorochemical-in-water dispersions, *Ann. NY Acad. Sci.* 589 (1990) 283–300.
- [49] E.S. Basheva, S. Stoyanov, N.D. Denkov, K. Kasuga, N. Satoh, K. Tsujii, Foam boosting by amphiphilic molecules in the presence of silicone oil, *Langmuir* 17 (2001) 969–979.
- [50] M. Vadekar, Oxygen contamination of hydrocarbon feedstocks, in: *In Refining, PTQ*, 2003, pp. 87–93.
- [51] H.M. van Sonsbeek, H. de Blank, J. Tramper, Oxygen transfer in liquid-impelled loop reactors using perfluorocarbon liquids, *Biotechnol. Bioeng.* 40 (1992) 713–718.
- [52] E. Dumont, Y. Andrès, P. Le Cloirec, Enhancement of oxygen transfer in bioprocess by the use of an organic phase: effect of silicone oil on volumetric mass transfer coefficient of oxygen ($k_L a$), in: Kennes, Veiga (Eds.), *Biotechniques for Air Pollution Control*, Universidade da Coruña, 2005, pp. 163–170.
- [53] E. Dumont, Y. Andrès, P. Le Cloirec, *Chem. Eng. Sci.*, in press.
- [54] S. Gillot, F. Kies, C. Amiel, M. Roustan, A. Héduit, Application of the off-gas method of the measurement of oxygen transfer in biofilters, *Chem. Eng. Sci.* 60 (2005) 6336–6345.
- [55] S. Capela, S. Gillot, A. Héduit, Comparison of oxygen-transfer measurement methods under process conditions, *Water Environ. Res.* 76 (2004) 183–188.
- [56] K. Fujie, K. Tsuchiya, L.-S. Fan, Determination of volumetric oxygen transfer coefficient by off-gas analysis, *J. Ferment. Bioeng.* 77 (1994) 522–527.
- [57] K. Van’t Riet, Review of measuring methods and results in nonviscous gas–liquid mass transfer in stirred vessels, *Ind. Eng. Chem. Process Des. Develop.* 18 (1979) 357–364.
- [58] G.D. Zhang, W.F. Cai, C.J. Xu, M. Zhou, A general enhancement factor model of the physical absorption of gases in multiphase systems, *Chem. Eng. Sci.* 61 (2006) 558–568.
- [59] E.S. Basheva, D. Ganchev, N.D. Denkov, K. Kasuga, N. Satoh, K. Tsujii, Role of betaine booster in the presence of silicone oil droplets, *Langmuir* 16 (2000) 1000–1013.
- [60] A. Morao, C.I. Maia, M.M.R. Fonseca, J.M.T. Vasconcelob, S.S. Alves, Effect of antifoam addition on gas–liquid mass transfer in stirred fermenters, *Bioprocess Eng.* 20 (1999) 165–172.
- [61] Y. Kawase, M. Moo-Young, The effect of antifoam agents on mass transfer in bioreactors, *Bioprocess Eng.* 5 (1990) 169–173.