Enhancement of oxygen transfer in bioprocesses by the use of an organic phase: effect of silicone oil on volumetric mass transfer coefficient of oxygen (k_La)

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ABSTRACT. The absorption of oxygen in water-silicone oil emulsions was studied in laboratory-scale bubble reactors at constant gas flow rate for the whole range of emulsion compositions (0-10% v/v). The volumetric mass transfer coefficients to the emulsions were experimentally measured using a dynamic absorption method. It was assumed that the gas phase contacts preferentially the water phase. It was found that addition of silicone oil hinders oxygen mass transfer compared to air-water system. Decreases of k_La up to 25% have been noted. Such decreases of the oxygen mass transfer coefficient which imply longer aeration times to transfer oxygen could represent a limiting step for biotechnological processes strongly depending on oxygen concentration. Nevertheless, as the large affinity of silicone oil for oxygen makes possible to increase the amounts of oxygen to be transferred from the gas phase, it appears that addition of more than 5% silicone oil should be beneficial to increase the oxygen transfer rate.

1 INTRODUCTION

Volatile organic compounds (VOC) are widely used in the industrialized countries as solvents. Therefore, the removal of VOC from waste air is of great interest and biological techniques are highly cost-effective for the treatment of waste gases containing low concentration of pollutants (<5 g/m^3). Microorganisms are capable of degrading a variety of VOC to harmless substances such as carbon dioxide, water and cell components. However, a major problem in the use of microbiological process for the degradation of VOC is the low solubility of these substances in water. Some VOC are also toxic to microorganisms. To overcome these problems, a water-immiscible organic liquid in which VOC show a high solubility can be used. Several organic liquids have been studied to treat VOC such as decane, dodecane, n-hexadecane, heptamethylnonane, 2-undecanone, silicone oil, oleyl alcohol, 1-octadecene (Daugulis, 2001). The organic liquid acts as a non-biodegradable liquid phase in which COV are dissolved and could diffuse into the aqueous phase. The microorganisms transform or degrade the substrate at the interface or in the aqueous phase. In addition to improving the absorption rate of VOC, the organic liquid is also assumed to act as oxygen vector in order to enhance the oxygen transport to the microorganisms. However, experimental

results from literature have shown that the use of organic liquid do not systematically lead to mass transfer enhancement of oxygen (Dumont and Delmas, 2003).

The aim of the present paper is to experimentally measure the volumetric mass transfer coefficient ($k_L a$) of oxygen in emulsions of water/silicone oils using a dynamic method. Silicone oils have been chosen for this study on the grounds that they have been largely tried to enhance elimination of numerous VOC from gases (table 1). Moreover, in our knoledge, there are no experimental $k_L a$ measurements available from literature.

Table 1. Studies using silicone oils to enhance elimination of volatile organic compounds.

References	Pollutants	Microorganisms
Lebeault (1990)	toluene	mixed culture
Cesario et al. (1992)	2-butanol; butylacetate; ethylmethylketone; toluene; hexane	
El Aalam et al. (1993)	styrene	Pseudomonas aeruginosa
Ascon-Cabrera and Lebeault (1995)	ethyl butyrate	Candida sp. CF3
Lebeault et al. (1996)	styrene	Pseudomonas aeruginosa Pseudomonas putida
Budwill and Coleman (1997)	hexane	microbial consortium
van Groenestijn and Lake (1999)	hexane	
Gardin et al. (1999)	xylene; butyl acetate	mixed culture
Hekmat and Vortmeyer (2000)	methyl ethyl benzene diethyl benzene	mixed culture
Fazaelipoor and Shojaosadati (2002)	hexane (80%) + hydrocarbons	
Aldric et al. (2004)	isopropyl-benzene	Rhodococcus erythropolis T902

2 MATERIALS AND METHODS

2.1 Chemicals

Silicone oils (Rhodorsil® fluids 47V5 and 47V10; dimethylpolysiloxane) have been purchased from Rhodia company. Experiments have been carried out using several emulsion compositions varying from 0 to 10% oil.

	Viscosity (25°C)	Density (25°C)	Surface tension (25°C)
Rhodorsil® fluids 47V5	5 mPa.s	910 kg/m^3	19.7 mN/m
Rhodorsil® fluids 47V10	10 mPa.s	930 kg/m^3	20.1 mN/m

2.2 Equipment

A schematic overview of the experimental set-up is given in figure 1. The reactor used have a 11.5 liters total volume (height 0.33 m, diameter 0.21 m). In the experiments, air is supplied from compressor and sparged through a distributor. The superfical velocity of gas (u_G) is 0.01 m/s (gas flow rate Q_G=3.3 10^{-4} m^3/s). All experiments are carried out at a constant temperature of 20°C maintained by the jacket. A dynamic method measuring the change of oxygen concentration in the gas phase is used to determine $k_L a$. The operation is batchwise with the respect to the liquid system (emulsion volume: V_L=10 L) and a constant volume of gas (V_G=2 L) is continuously flowing through the

liquid. The oxygen fraction in the gas phase is determined using a paramagnetic oxygen analyser (Cosma Cristal 300). The flow rate of gas to the oxygen analyser is quite negligible compared to the total gas flow rate in the reactor (0.2%). Each experiment is carried out according to the following procedure:
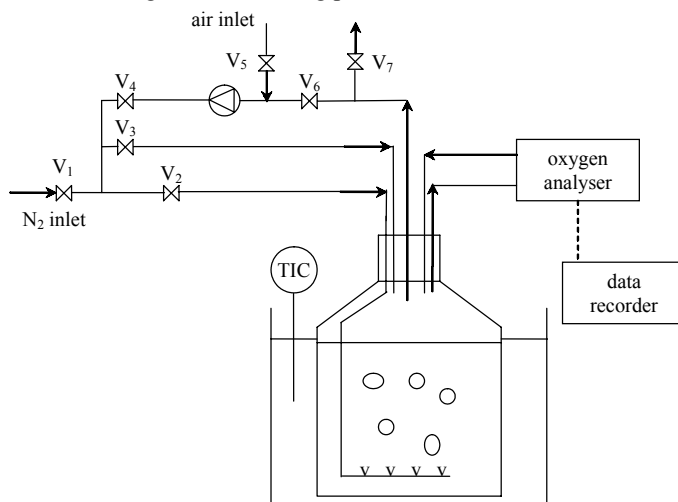

Figure 1. Schematic overview of the experimental set-up used to determine $k_L a$.

1) the dissolved oxygen in the emulsion is removed during 10 minutes by sparging nitrogen supplied from a nitrogen cylinder (V_1, V_2, V_7 opened; V_6, V_4, V_3 closed). Desorbed oxygen and nitrogen go out through valve V_7,

2) the volume above the liquid and all the other volumes occupied by the gas are renewed by means of the compressor with atmospheric air without disturbing the liquid (V_3, V_4, V_5 opened; V_1, V_2, V_6 closed). After confirming from the reading of the oxygen sensor that the volume occupied by the gas is totally filled with air, valves V_3, V_5 and V_7 are closed and valves V_2 and V_6 are opened simultaneously,

3) the finite volume of air is sparged through the reactor and decrease in oxygen concentration in air is monitored and recorded as a function of time for further analysis.

Before doing experiment for each emulsion, the reactor in cleaned with alcohol then distilled water.

3 $k_L a$ CALCULATION

3.1 Assumptions

The dynamic method for $k_L a$ measurement in air-water-silicone oil systems 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 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 (Van't Riet, 1979). Then, the overall mass transfer coefficient is considered as the liquid phase mass transfert coefficient $k_L a$.

3. Liquid phase is perfectly mixed. This may be assumed considering the convective recirculation and turbulence caused by the rising gas bubbles leading to a mixing time much shorter than the characteristic mass transfer time $1/k_La$.

4. Gas phase is considered as plug flow in the closed flowing circuit as in the oxygen analyser circuit.

5. The presence of silicone oil in the emulsion does not change 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 <5 s which is smaller than the mass transfer response time of system: $1/k_La$.

3.2 Derivation of k_La

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 silicone oil phase (dispersed liquid phase).

$$-V_G \frac{dC_{gas}}{dt} = V_L\,(1-\phi)\,\frac{dC_{water}}{dt} + V_L\,\phi\,\frac{dC_{oil}}{dt} \tag{1}$$

V_L is the total volume of the liquid phase and V_G the total volume of the gas phase. C_{water} and C_{oil} are the concentrations of oxygen in water and silicone oil phases respectively. Ø is the dispersed liquid phase hold-up (volume of organic liquid phase as a fraction of total liquid phase volume).

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

$$C_{oil} = m_R\,C_{water} \tag{2}$$

m_R is the solubility ratio defined as the ratio of the solubility of oxygen in the silicone oil to that in the water. Oxygen dissolves approximately seven times better in silicone oil than in water.

Equations (1) and (2) lead to:

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

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

$$C_{gas} = \frac{P}{RT}\,y_{oxygen} \tag{4}$$

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, equation (5) is obtained from equation (4):

$$\frac{dC_{gas}}{dt} = \frac{P}{RT}\,\frac{dy_{oxygen}}{dt} \tag{5}$$

Combining equations (5) and (3) gives after integrating between t=0 (C_{water}=0 and y_{oxygen}=$y_{oxygen(t=0)}$) and t:

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

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

$$-V_G \frac{P}{RT} \frac{dy_{oxygen}}{dt} = k_L a \, V_L \left(C^*_{water} - C_{water} \right) \qquad (7)$$

where C^*_{water} is the equilibrium concentration between water and the absorbed gas phase. C^*_{water} is defined according to equation (8) where p_{oxygen} is the partial pressure of oxygen in the gas phase and H is the Henry constant for oxygen in water:

$$C^*_{water} = \frac{p_{oxygen}}{H} \qquad (8)$$

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

$$C^*_{water} = \frac{P}{H} \frac{p_{oxygen}}{P} = \frac{P}{H} y_{oxygen} \qquad (9)$$

Introducing the expression of C_{water} and C^*_{water} in equation (7) gives:

$$-\frac{V_G}{V_L} \frac{P}{RT} \frac{dy_{oxygen}}{dt} = k_L a \left[\frac{P}{H} y_{oxygen} + \frac{V_G}{V_L} \frac{1}{[1+\phi(m_R-1)]} \frac{P}{RT} \left(y_{oxygen(t)} - y_{oxygen(t=0)} \right) \right] \qquad (10)$$

whose integration between t=0 and t gives:

$$\left[\frac{1}{\alpha + \dfrac{1}{1+\phi(m_R-1)}} \right] \ln \left\{ \frac{\alpha \, y_{oxygen(t=0)}}{\left[\alpha + \dfrac{1}{1+\phi(m_R-1)} \right] y_{oxygen(t)} - \dfrac{y_{oxygen(t=0)}}{1+\phi(m_R-1)}} \right\} = k_L a \, t \qquad (11)$$

with $\alpha = \dfrac{V_L RT}{V_G H}$. By plotting the left member (called f(t)) of equation (11) versus time,

we obtained a straight line whose the slope gives the volumetric mass transfer coefficient $k_L a$ for the aqueous phase in the presence of silicone oil. Introducing Ø=0 in equation (11) allows the determination of $k_L a$ value in binary air-water system.

4 EXPERIMENTAL RESULTS AND DISCUSSION

4.1 $k_L a$ measurement in binary air-water system (reference system)

Thirty nine measures have been carried out in the case of the binary air-water system. Figure 2 shows an exemple of the monitored decrease of the mole fraction of oxygen (y_{oxygen}) in the gas phase versus time. From these experimental data, determination of $k_L a$ (called $k_L a^{ref}$ for the binary system) is obtained (Figure 3) by using equation (11). For our apparatus and the hydrodynamic conditions (u_G = 0.01 m/s), $k_L a$ values range from 0.0132 to 0.0178 s^{-1} (mean value $k_L a^{ref}$: 0.0156 s^{-1}; standard deviation 15%).

4.2 $k_L a$ measurement in the presence of silicone oil

Experiments have been carried out in triple using several emulsion compositions varying from 0 to 10% silicone oil. Figure 3 shows the calculation of the volumetric mass transfer coefficient for a multiphasic system (called $k_L a^*$) containing 1% silicone oil 47V5. In this example, addition of silicone oil leads to a decrease of volumetric mass transfer coefficient by about 25%.
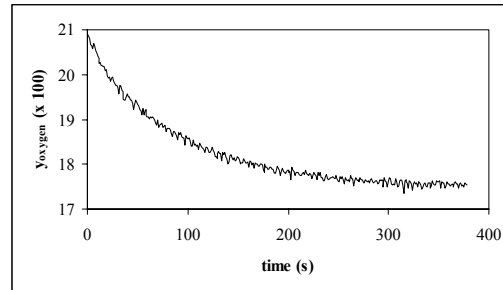
Figure 2. Example of the decrease of the mole fraction of oxygen in the gas phase versus time
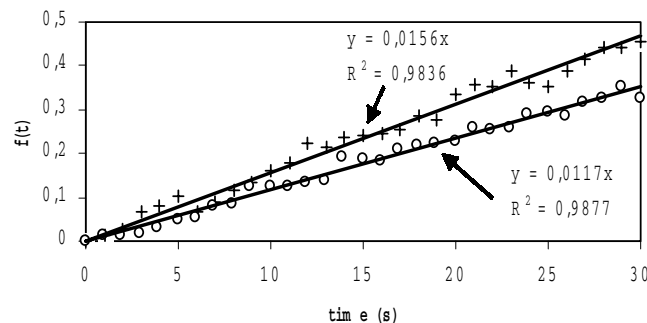for a binary air-water system.

Figure 3. Example of k_La determination according to equation (11) obtained from experimental
measurement presented at Figure 2. (+) air-water reference system; (○) air-water-1% silicone oil
47V5.

Figure 4 presents relative k_La measurements (k_La^*/k_La^{ref}) for the whole of the
experiment as a function of emulsion composition for both silicone oils used. Addition
of silicone oils hinders oxygen mass transfer compared to air-water system. Mass
transfer coefficient initially decreases rapidly and then increases rather slowly with
increasing oil volume fraction. Effects are particularly strong for low volume fraction of
silicone oils (1-2%) and are more important for the most viscous silicone oil (47V10).
Similar results have been reported in literature in the case of others organic liquids used
as oxygen vectors. Yoshida *et al.* (1970) have observed such variation of relative k_La
when using toluene and oleic acid. By adding n-dodecane, Hassan and Robinson (1977)
have shown that (k_La^*/k_La^{ref}) was always less than unity for oil fraction in the range
1%<Ø<10%. They reported that as Ø was increased from 0 to 1%, (k_La^*/k_La^{ref})
decreased sharply to about 0.8, increased slightly as Ø increased to 6%, and leveled off
at an average value up to 10%. Results described by Hassan and Robinson (1977) are
very closed to the results presented at Figure 4. More recently, Nielsen *et al.* (2003)
clearly indicated that as the fraction of hexadecane in the bioreactor was increased, the
experimental value of k_La decreased. Generally speaking, reported experimental oxygen
absorption results in the literature show that the k_La value can decrease, remain
unaffected or increase upon addition of the organic phase (Dumont and Delmas, 2003).
Several explanations based on the change of the physical properties of the emulsion
(density, viscosity, gas solubility, gas diffusivity) due the organic phase addition have
been proposed. Interfacial properties of the emulsion, particularly the spreading
coefficient, have been used to explain the variations in the volumetric mass transfer

coefficient with the fraction of the organic phase. However, studies devoted to the influence of the spreading coefficient have led to contradictory results (see Dumont and Delmas, 2003). To date, influence of small amounts of organic phases on mass transfer is considerable, but a satisfactory description of the phenomenom is still lacking.
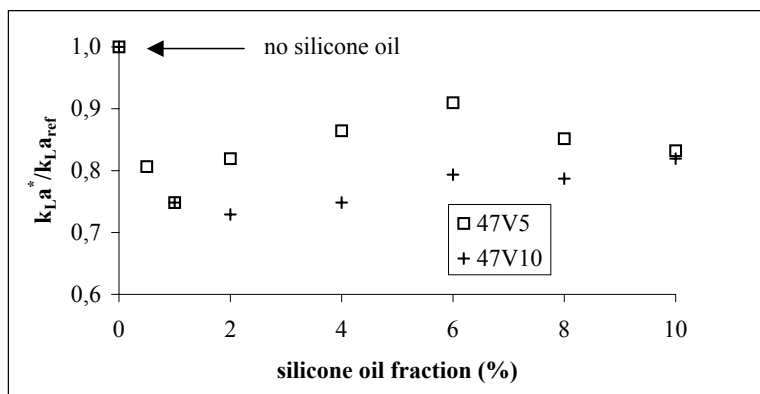

Figure 4. Relative $k_L a$ values for oxygen absorption in emulsions of water-silicone oils as a function of silicone oil fraction (u_G = 0.01 m/s).

Decrease of the oxygen mass transfer coefficient due to silicone oil addition could be very crucial in many cases of biotechnological processes, particularly those which depend strongly on oxygen concentration. Then, opposite silicone oil addition effects must be considered. On the one hand, the decrease of the $k_L a$ with silicone oil addition implies longer aeration times to saturate. But, on the other hand, the presence of silicone oil having a large affinity for oxygen (m_R=7) makes it possible to increase the amounts of oxygen to be transferred from the gas phase. Consequently, it is possible to propose an optimal fraction of oil to maximize the rate of oxygen mass transfer to the system. In our study, assuming that the maximum decrease in $k_L a^*$ is about 25% referring to a system without oil, 5% silicone oil addition will be enough to begin to enhance the oxygen mass transfer rate. Reported results from literature indicate that silicone oil addition should be a good strategy to enhance the removal efficiency for hydrophobic compounds poorly soluble in water. Hekmat and Vortmeyer (2000) measured the stationary degradation kinetics of volatile aromatic compounds in a laboratory-scale trickle-bed bioreactor. They shown that the addition of 10% silicone oil resulted in a 2.4-fold increase of the degradation rate. Aldric *et al.* (2004) reported the interest of use silicone oil at a rate of 10% in a biphasic bioreactor. These authors showed that silicone oil makes it possible to absorb a large quantities of isopropyl-benzene within the medium of biological abatement. Budwill and Coleman (1997), developing a biofilter with 20% silicone oil, observed an increase in n-hexane removal over that in the untreated control. Conversely, Fazaelipoor and Shojaosadati (2002), which investigated the effect of using silicone oil in the bed of a perlite biofilter for removal of a mixture of hydrophobic compounds, showed that inclusion of 20% silicone oil in biofilter only slightly increases removal efficiency of VOC. However, some parameters such as microbial activity and moisture content must also be considered in such biofiltration process (Budwill and Coleman, 1997).

5 CONCLUSIONS

Volumetric mass tranfer coefficient ($k_L a$) of oxygen in gas-water-silicone oil systems have been experimentally measured using a dynamic method. Addition of silicone oils hinder oxygen mass transfer compared to air-water system. Decreases of $k_L a$ up to 25% have been noted. Such decreases of the oxygen mass transfer coefficient could represent a limiting step for biotechnological processes strongly depending on oxygen concentration. Nevertheless, as silicone oil presents a large affinity for oxygen (seven times higher than water), makes it possible to increase the amounts of oxygen to be transferred from the gas phase, addition of more than 5% silicone oil should be beneficial to increase the oxygen transfer rate. Future investigations devoted to oxygen transfer rate (OTR) in presence of biomass will lead in order to quantify the influence of silicone oil addition on COV biodegradation.

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