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Mass Transfer Characteristics in Gas-liquid-liquid System

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Gas-liquid-liquid systems are used in aerobic bioprocesses, biological waste water treatment and liquid phase heterogenisation in catalysis by coordination complexes (biphasic catalysis). Biphasic catalytic systems are used because of the easy separation of the catalysts from the organic products (as the catalyst is soluble in the aqueous phase only). In such media a significant increase of the gas-aqueous liquid mass transfer rate has been observed (Lekhal et al., 1997). Mass transfer behaviour is important for the gas-liquid-liquid reaction system with fast parallel and consecutive reactions, as its effect on the product yield can be significant (Brilman, 1998). For systems with slow reaction kinetics, it will not create any problem as the three phases will be at physical equilibrium.

A review of mass transfer enhancement in gas-liquid-liquid systems has been reported recently by Dumont and Delmas (2003). In bioprocesses, one inert immiscible organic liquid is added for the purpose of mass transfer enhancement of oxygen into aqueous media owing to the imbalancing situation between low solubility of oxygen in aqueous media and high demand of oxygen of micro-organisms in aqueous phase (Ju et al., 1991). In this way, the oxygen transfer rate from the gas phase to continuous liquid phase can be increased without increasing power input, which ultimately can damage the cell structure. However, the addition of a second immiscible organic liquid may also decrease mass transfer, despite higher oxygen solubility (up to 20 times) in these organic liquids than in water (Lu-Kwang and Chester, 1989).

The effect of addition of a dispersed liquid phase on mass transfer parameters like gas hold-up, interfacial area and mass transfer coefficient has been studied occasionally. However, no general results could be derived. Yoshida et al. (1970) studied the effect of the addition on volumetric mass transfer coefficient ($k_L a$) of different second immiscible liquid phases (organic) in aqueous phase. They found the decrease of $k_L a$ with the increase of hold-up of kerosene and paraffin; they also reported an initial decrease followed by an increase with the increase of dispersed liquid phase hold-up in the case of oleic acid and toluene in an agitated reactor. Linek and Benes (1976) also reported such variation of $k_L a$ for oleic acid. Cents et al. (2001) observed an initial decrease of $k_L a$ when adding 1-octanol and toluene as a dispersed organic phase. They found that the initial decrease in $k_L a$ on the addition of toluene was completely due to a decrease in the interfacial area (a). In the case of 1-octanol, the initial decrease in $k_L a$ was completely due to a decrease in the value of

Experimental results of mass transfer in air-water system with a dispersed immiscible organic liquid in a bubble column 0.076 m in diameter for seven different organic liquids at various hold-up are presented. Experiments are carried out at gas superficial velocity in the range 0.0052-0.026 m/s at 293 K. The volumetric mass transfer coefficient, $k_L a$ is determined by dynamic gas absorption technique. Overall gas hold-up is also measured. Slight addition of n-decane, dodecane and n-heptane in air-water medium significantly enhances mass transfer from the gas phase, to the continuous aqueous phase whereas toluene, anisole and 2-ethyl-1-hexanol retard mass transfer.

On présente des résultats expérimentaux de transfert de matière dans un système air-eau avec un liquide organique non miscible dispersé dans une colonne à bulles de 0,076 m de diamètre intérieur pour différents liquides organiques à différentes rétentions. Les expériences sont menées pour des vitesses de gaz superficielles de 0,0052-0,026 m/s à 293 K. Le coefficient de transfert de matière volumétrique, $k_L a$, est déterminé par la technique d'absorption de gaz dynamique. La rétention de gaz globale est également mesurée. Un léger ajout de n-décane, dodécane et n-heptane dans le milieu air-eau augmente significativement le transfert de matière de la phase gazeuse à la phase aqueuse continue, tandis que le toluène, l'anisole et l'éthyle-2-hexanol-1 retardent le transfert de matière.

Keywords: gas-liquid-liquid, bubble column, dispersed liquid, mass transfer enhancement.

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the mass transfer coefficient k_L . At higher dispersed fractions both organic components enhanced mass transfer. Cents et al. (2001) also observed that the addition of dodecane and heptane caused the decrease of $k_L a$. Sharma and Mashelkar (1968) showed the marginal increase of effective interfacial area (a) and considerable reduction of mass transfer coefficient (k_L) when adding 2-ethyl hexanol (0-15%).

The enhanced absorption rate may be caused by changes in the gas-liquid interfacial area a , through gas phase hold-up and mean bubble size variation, or by increasing the liquid side mass transfer coefficient, k_L . Eckenfelder and Barnhart (1961) reported the increase of both k_L and $k_L a$ with the addition of organic substances after the initial decrease of k_L , whereas Linek and Benes (1976) reported a constant value of k_L when adding n -alkanes and a slight increase of k_L after a sharp decrease when adding oleic acid. Cents et al. (2001) assumed a constant value of k_L under the same hydrodynamic condition and power dissipation. So, from the above literature we can conclude that the addition of an immiscible organic liquid phase to a gas-aqueous liquid phase system may have complex effects and may significantly influence oxygen transfer by absorbing oxygen or supplying it to other phases, or by influencing the fluid mechanics of the continuous phase, thereby influencing mass transfer coefficient and interfacial area of the continuous phase. The effects reported on mass transfer parameters, like gas-liquid interfacial area and gas hold-up, are discussed shortly. No general trends can be derived from the reported results in the literature. Though many studies have been reported on gas-liquid-liquid measurements performed in stirred vessels, specific information with G-L-L system in bubble columns is quite limited (Yoshida et al., 1970; Sharma and Mashelkar, 1968; Kato et al., 1985).

In the present paper, volumetric mass transfer coefficient $k_L a$ and overall gas hold-up in gas-liquid system are measured in a bubble column adding seven different immiscible organic liquids as a droplet dispersed phase. Oxygen solubility is significantly higher in these organic liquids than in water. Mass transfer characteristics are also analysed in terms of mass transfer enhancement in G-L-L system and possible explanations are given.

Table 1. Physical characteristics of the organic liquids used in the experiments (293K).

Name of organic liquids	m_R	Density (kg/m ³)	Viscosity (mPa-s)	Surface tension (mN/m)	$\sigma^*_{water-air}$ mN/m
Toluene (C ₇ H ₈)	8.2	869.5	0.582	28.53	44
Anisole (C ₇ H ₈ O)	5.6	995.0	1.092	35.61	65
2-ethyl-1-Hexanol (C ₈ H ₁₈ O)	7.5	833.5	7.088	30.54	43
Decyl Alcohol (C ₁₀ H ₂₂ O)	4.9	829.0	13.684	28.76	38
Dodecane (C ₁₂ H ₂₆)	8.1	748.6	1.526	25.41	71
n -Decane (C ₁₀ H ₂₂)	8.8	746.7	0.932	23.90	67
n -Heptane (C ₇ H ₁₆)	10.9	686.0	0.412	20.30	65

Experimental Apparatus and Procedure

Figure 1 shows the experimental set-up used here. The inner diameter of the bubble column reactor (1) is 0.076 m and the total height of the liquid (without gas) is 1.95 m (volume of liquid: $V_L = 0.0092 \text{ m}^3$). In the experiments, air is supplied from compressor (4), and sparged through a distributor with 20 holes (hole diameter: 0.0005 m) in a square pitch having a pitch distance of 0.004 m. The superficial velocity of gas (u_g) varies in the range of 0.0052-0.026 m/s. All the experiments are carried out at a constant temperature of 293 K maintained by the jacket (2).

Seven different immiscible organic liquids have been used in the experiment. The physical characteristics of the organic liquids are shown in Table 1. The data of viscosity and surface tension value are taken from Yaws (1999). The data of the solubility ratio m_R (with reference to oxygen solubility in water) of the different liquids listed are taken from Brillman (1998), except the solubility ratio of n -decane, anisole and decyl alcohol, which is calculated from the value of Ostwald coefficient given by Battino (1981). It has been found that the interfacial properties of the continuous aqueous phase changed due to solubility of oil (though these organic liquids have very low solubility, e.g., solubility of toluene in water is 515 $\mu\text{g/mL}$ at 293 K. The interfacial tension in terms of saturated condition of the second liquid phase ($\sigma^*_{water-air}$) is then measured with the help of tensiometer (Kruss GmbH, model: K6). After mixing the two liquid phases and long time stirring, the two phases were separated and surface tension for each liquid phase was measured.

The operation is batchwise with respect to the liquid system. Though the gas is continuously flowing through the liquid, it has a constant volume in this closed system. The flow rate of gas to the oxygen sensor (through rotameter 6) is quite negligible (maximum: 0.07%) compared to the total gas flow rate in the column. The dissolved oxygen in water is removed within 30 minutes by sparging nitrogen supplied from a nitrogen cylinder, desorbed oxygen and nitrogen going out through

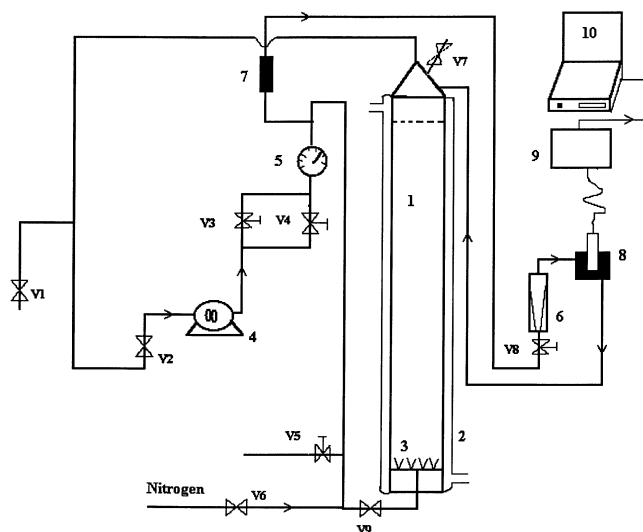


Figure 1. Experimental set-up (1. Bubble column reactor, 2. Jacket, 3. Gas distributor, 4. compressor, 5. Magnetic flow meter for gas, 6. Gas rotameter, 7. Mist eliminator, 8. Oxygen electrode, 9. Recorder, 10. PC).

valve V1. When the reading in oxygen sensor (8) (Orbisphere, indicating instrument: model 3660 and oxygen sensor: model 31120A) is zero, then the supply of the nitrogen is stopped by closing simultaneously valve V6 and valve V1. Then the volume above the liquid column and all the other volumes occupied by gas are renewed with atmospheric air without disturbing the liquid column by opening valves V5 and V7 and closing valve V9. After confirming from the reading of the oxygen sensor, that the volume occupied by gas is totally filled with air, the compressor is stopped, valves V5 and V7 are closed, and valve V9 is opened. Then the finite volume of air is sparged through the liquid column by means of the compressor. Different superficial gas velocities can be selected. Decrease in oxygen concentration in air is monitored as a function of time through the recorder (9) (connected to the oxygen electrode) and the data is transferred to the computer (10) for further analysis. The overall gas hold-up is calculated from the variation of position of the free surface in the aerated and non-aerated column. Before doing experiment for each organic liquid, the column is thoroughly cleaned.

Theory for Evaluation of $k_L a$

Assumptions

In the reactor the ideal gas law is applicable to calculate the number of moles of gas absorbed by liquid. The operating conditions justify such an assumption, since temperature and pressure are low.

1. 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 $1/k_L a$.
2. The response time for the oxygen sensor used is 7 s. This can be neglected as the total time for observing steady value of oxygen concentration is in the range of ~ 180 s, meaning that $1/k_L a$ is much higher than this response time.
3. Overall mass transfer coefficient is considered as the liquid phase mass transfer coefficient for oxygen absorption as the value of gas phase volumetric mass transfer coefficient is very large compared to that in liquid phase (6 to 24 times) (Kojima et al., 1997).
4. The dispersed organic phase does not change Henry constant for oxygen in water.
5. There is no direct contact between the gas and the organic liquid phase.
6. Liquid-liquid equilibrium in terms of oxygen concentration is assumed during absorption as liquid-liquid mass transfer is very fast compared to gas-liquid mass transfer.

Derivation of $k_L a$

In the gas-liquid-liquid system, the total change in concentration of oxygen in air (C_G) is due to the amount of oxygen absorbed in the continuous liquid phase and to the amount of oxygen absorbed in the dispersed liquid phase.

$$-\frac{d[C_G(t)V_G]}{dt} = V_L(1-\phi_{disp})\frac{dC_W}{dt} + V_L\phi_{disp}\frac{dC_O}{dt} \quad (1)$$

V_L is the total volume of liquid phase and V_G the total volume of gas phase (V_L and V_G are constant); C_W and C_O denote the

concentration of oxygen in water and in dispersed organic phase respectively. ϕ_{disp} is the dispersed liquid phase hold-up (volume of organic liquid phase as a fraction of total liquid phase volume).

As these two liquid phases are assumed to be in equilibrium at any time (assumption 6):

$$C_O = m_R C_W \quad (2)$$

m_R is the solubility ratio defined as the ratio of the solubility of oxygen in the organic phase to that in the aqueous phase.

Equation (1) and (2), lead to:

$$-\frac{d[C_G(t)]}{dt} = \frac{V_L}{V_G} (1-\phi_{disp} + m_R\phi_{disp}) \frac{dC_W}{dt} \quad (3)$$

$C_G(t)$ for the constant volume of liquid and gas can be obtained from mass balance:

$$C_G(t) = \frac{P}{RT} X(t) \quad (4)$$

the mole fraction $X(t)$ is measured by the oxygen sensor of oxygen in gas phase; P is the total pressure in gas phase considered constant during the experiment, and calculated as a mean value between top and bottom values in the column.

After differentiating with respect to time t , we get from the above equation:

$$\frac{d[C_G(t)]}{dt} = \frac{P}{RT} \frac{dX(t)}{dt} \quad (5)$$

From (3) and (5) the following equation is stated for a system of constant volume of gas and liquid:

$$-\frac{V_G}{V_L} \frac{P}{RT} \frac{dX(t)}{dt} = (1-\phi_{disp} + m_R\phi_{disp}) \frac{dC_W}{dt} \quad (6)$$

Integrating (6) leads to:

$$C_W = -\frac{V_G}{V_L} \frac{P}{RT} \left[\frac{1}{1+\phi_{disp}(m_R-1)} \right] (X(t) - X(t=0)) \quad (7)$$

According to mass transfer conservation principle and to perfectly mixed behaviour of liquid, the overall mass transfer rate in gas-liquid system can be determined by:

$$-\frac{V_G}{V_L} \frac{P}{RT} \frac{dX(t)}{dt} = k_L a [C_W^*(t) - C_W] \quad (8)$$

where $C_W^*(t)$ is the equilibrium concentration between the continuous liquid phase (water) and the absorbed gas phase (according to assumption 5: no direct contact between the gas and the organic liquid phase).

The partial pressure of oxygen in gas phase is defined by:

$$p = H C_W^* \quad (9)$$

Dividing by the total pressure P:

$$\frac{p(t)}{P} = \frac{H}{P} C_W^*(t) \quad (10)$$

$p(t)/P$ can be expressed as the mole fraction $X(t)$.
So,

$$\text{So, } C_W^*(t) = \frac{P X(t)}{H} \quad (11)$$

Introducing the expression of C_W and $C_W^*(t)$ in Equation (8), we get:

$$-\frac{dX(t)}{dt} = k_L a \left[X(t) \left(\frac{V_L RT}{V_G H} + \frac{1}{1 + \phi_{disp}(m_R - 1)} \right) - \frac{X(t=0)}{1 + \phi_{disp}(m_R - 1)} \right] \quad (12)$$

$$\text{With } \left(\frac{V_L RT}{V_G H} + \frac{1}{1 + \phi_{disp}(m_R - 1)} \right) = \gamma \text{ and } 1 + \phi_{disp}(m_R - 1) = \delta$$

in the above equation and by integrating it, we get:

$$\frac{1}{\gamma} \ln \left(\frac{X(t=0)(\gamma\delta - 1)}{\gamma\delta X(t) - X(t=0)} \right) = k_L a t \quad (13)$$

$$\text{By plotting } f(t) = \frac{1}{\gamma} \ln \left(\frac{X(t=0)(\gamma\delta - 1)}{\gamma\delta X(t) - X(t=0)} \right) \text{ versus } t,$$

the slope gives the value of the volumetric mass transfer coefficient ($k_L a$) for the aqueous phase in G-L-L system. We can also get the value of $k_L a$ of air water putting the value of $\phi_{disp} = 0$ in Equation (13).

$$\left(\gamma = \frac{V_L RT}{V_G H} + 1 \text{ and } \delta = 1 \right)$$

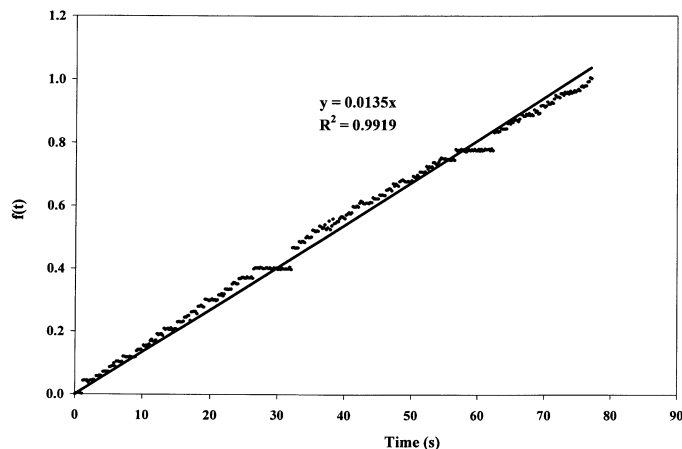


Figure 2. An example for $k_L a$ determination according to equation (15) in air-water system after the addition of 2-ethyl-1-hexanol ($\phi_{disp} = 0.1$ and $u_g = 0.011$ m/s).

For example, $f(t)$ versus t has been plotted for the system of air water plus 2-ethyl-1-hexanol ($\phi_{disp} = 0.1$) at a superficial gas velocity of 0.011m/s, from which $k_L a$ has been obtained as 0.0135 s^{-1} (Figure 2). For each superficial gas velocity in a definite dispersed phase liquid phase hold-up, the experiment was repeated for three times and the variation of $k_L a$ kept within $\pm 10\%$.

Calculation of Enhancement Factor (E)

The enhancement factor is defined as the ratio of absorption flux in the presence of a dispersed immiscible organic liquid phase to that in its absence, under the same hydrodynamic conditions and the same driving force:

$$E = \frac{N(\phi_{disp} > 0)}{N(\phi_{disp} = 0)} \quad (16)$$

This definition assumes the equilibrium at the interface between gas and continuous liquid phase stating that there is no direct contact between dispersed droplets and gas phase. For the calculation of flux (N), $X(t)/X(t=0)$ was plotted versus time. Then the slope of this curve was determined at time $t=0$ from which the initial flux was obtained. For example, Figure 3 shows $X(t)/X(t=0)$ versus time in air-water system with the addition of 2-ethyl-1-hexanol ($\phi_{disp} = 0.02$ and $u_g = 0.0052$ m/s). The initial slope of the curve ($t=0$) is 0.013 s^{-1} is very close to the estimated value of $k_L a$ (0.0135 s^{-1}) from the slope of the complete recording on Figure 2).

Results and Discussion

General Observations

Figure 4 shows the concentration graph $X(t)/X(t=0)$ versus t in air-water systems with the addition of seven immiscible organic liquids ($\phi_{disp} = 0.005$ and $u_g = 0.011$ m/s in all cases) in which oxygen is much more soluble than in water. In this figure the case of air-water system ($\phi_{disp} = 0$) has also been plotted. It is clear from this figure that the rate of change of oxygen concentration is slower with the addition of four organic liquids (toluene, anisole, 2-ethyl-1-hexanol and decyl alcohol)

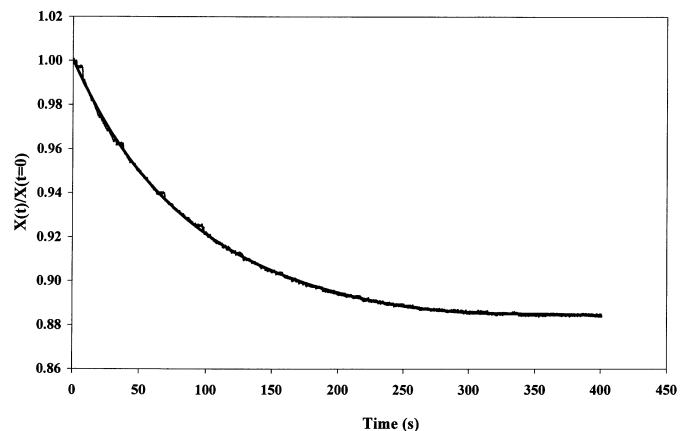


Figure 3. Example for the plot of normalized concentration curve $X(t)/X(t=0)$ versus time in air water after the addition of 2-ethyl-1-hexanol ($\phi_{disp} = 0.02$ and $u_g = 0.0052$ m/s) from which the flux of oxygen transfer at time, $t=0$ can be calculated.

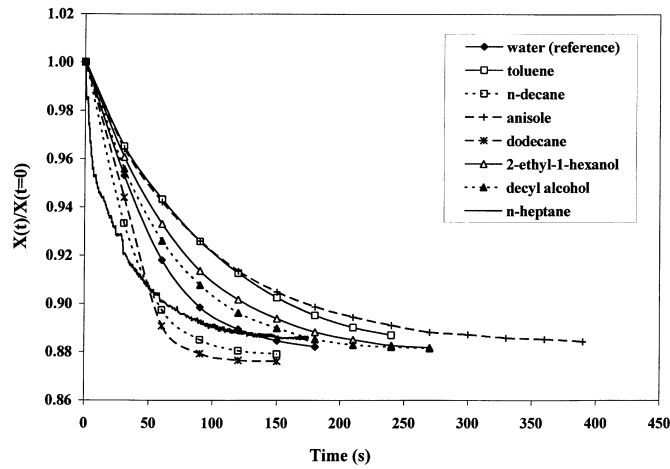


Figure 4. Concentration curves $X(t)/X(t=0)$ versus time) in air–water system after the addition of seven different immiscible organic liquids (in all cases, $\phi_{disp} = 0.005$ and $u_g = 0.011$ m/s).

compared to that of air water only ($\phi_{disp} = 0$). On the contrary, with *n*-decane, dodecane and *n*-heptane, the rate of change of oxygen concentration is faster than that of air water only.

For a more complete analysis of these results, bubble sizes or, at least, gas hold-up should be investigated. Figure 5 shows the overall gas hold-up in air water and in air water plus different immiscible organic liquids ($\phi_{disp} = 0.005$). Gas hold-up for G-L-L systems with *n*-decane, dodecane and *n*-heptane is higher at all superficial gas velocities with respect to air–water system, whereas toluene, 2-ethyl-1-hexanol and anisole lead to smaller gas hold-up, which explains the low variation of $X(t)/X(t=0)$ in these cases. It is also interesting to note the particular case of the addition of decyl alcohol for which gas hold-up is higher then lower to the gas hold-up for air water when increasing the superficial gas velocity.

The enhancement factor calculated from initial flux of oxygen has been plotted as a function of dispersed phase hold-up in Figure 6 at $u_g = 0.0052$ m/s. As expected from Figure 4, very different values (ranging from 0.4 to 7) are obtained depending on the nature and volume fraction of the dispersed organic phase. The three alkanes (*n*-decane, dodecane and *n*-heptane) strongly enhance gas–liquid mass transfer while on the contrary, toluene and 2-ethyl-1-hexanol always retard mass transfer.

This set of data is rather difficult to analyse. First, in any case, the enhancement factor increases when increasing the amount of immiscible organic liquid phase due to higher solubility of oxygen in the dispersed organic phase. However, this solubility effect can explain neither the kind of variations nor the values of the enhancement factor. Non-linear variations of the enhancement factor are noteworthy: significant enhancements are reached at very low organic fraction ($\phi_{disp} = 0.005$) and, in return, very few above $\phi_{disp} = 0.05$.

Comparison of Figure 6 on mass transfer and Figure 5 concerning gas hold-up measurements proves the enhancement of mass transfer to be connected with the increase of gas hold-up. This is presented in Figure 7 plotting all data at the lowest organic fraction: $\phi_{disp} = 0.005$. Nevertheless, it clearly appears

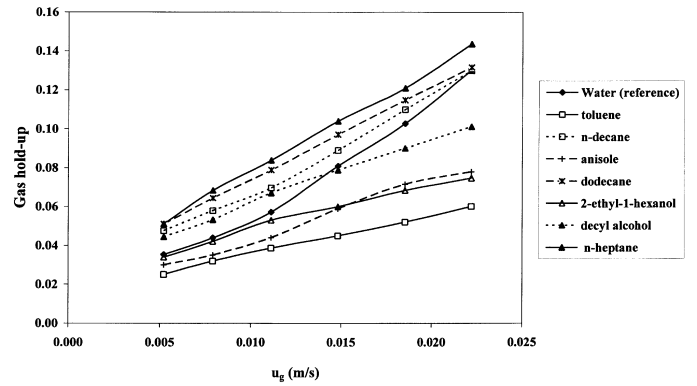


Figure 5. Gas hold-up characteristics in G-L-L systems with seven different immiscible organic liquids (in all cases, $\phi_{disp} = 0.005$).

that though $k_L a$ is roughly proportional to gas hold-up with the five organic liquids, it is much higher with alkanes than with toluene and 2-ethyl-1-hexanol, about threefold at same gas hold-up. So changes in gas hold-up may explain only a small part of the outstanding sensitivity of $k_L a$ to the addition of small amounts of organic phase.

From visual observations, the main effect of adding oil appears to be the change in bubble size. Very small bubbles are formed when alkanes are added even at low loading, $\phi_{disp} = 0.005$. On the contrary, adding toluene or 2-ethyl-1-hexanol results in very large deformed bubbles, several cm in diameter, rising faster and leading to lower gas hold-up. Both larger bubble diameter and lower gas fraction involve lower surface area, and then mass transfer reduction.

Influence of u_g and ϕ_{disp} on $k_L a$

Figure 8 shows the effect of superficial gas velocity on volumetric mass transfer coefficient for air water ($\phi_{disp} = 0$) and air–water–oil media (at $\phi_{disp} = 0.01$). As usual, $k_L a$ increases with the increase of superficial gas velocity, which is mainly due to increase in interfacial area. As expected from Figure 6, $k_L a$ values of air–water–oil systems with *n*-decane, dodecane and *n*-heptane are larger than that of air water and those of toluene and 2-ethyl-1-hexanol are smaller. As mentioned, from visual

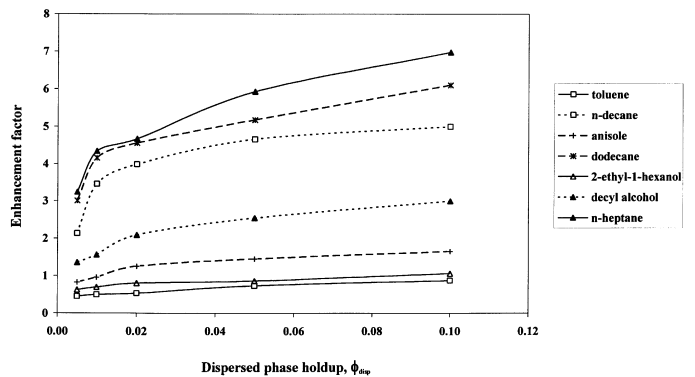


Figure 6. Effect of oil concentration on the enhancement factor in air–water–oil systems ($u_g = 0.0052$ m/s).

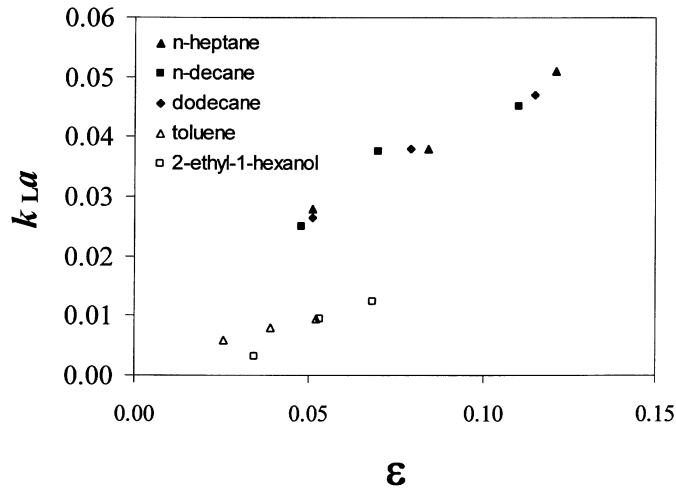


Figure 7. $k_L a$ vs gas hold up at $\phi_{disp} = 0.005$.

observations, the enhancement of mass transfer seems mainly due to an increase in gas-water interfacial area which should depend on some properties of the added oils. Table 1 gives the evolution of the air-water surface tension for water saturated with oil ($\sigma_{water-air}^*$). Compared with air-water (pure water) surface tension ($\sigma_{water-air} = 72.8$ mN/m), oil addition leads systematically to a reduction of surface tension. As expected, this reduction is very limited in the case of alkanes, due to their very poor solubility in water. On the other hand, the largest effect of oil addition on surface tension is obtained with organic liquids slightly soluble in water but leading surprisingly to large bubbles and having no effect or negative effect on mass transfer rate. Furthermore, addition of *n*-heptane and anisole, which leads to the same value of the air-water surface tension ($\sigma_{water-air}^* = 65$ mN/m) gives opposite results of mass transfer (Figure 4) and gas hold-up (Figure 5). Previously, some mass transfer enhancements in G-L-L systems had been explained in terms of spreading coefficient (Yoshida et al., 1970), which is defined as the difference between the surface tension of air water and the summation of surface tension of air-oil and oil-water phase (details in Dumont and Delmas, 2003): a system with positive spreading coefficient would lead to enhancement.

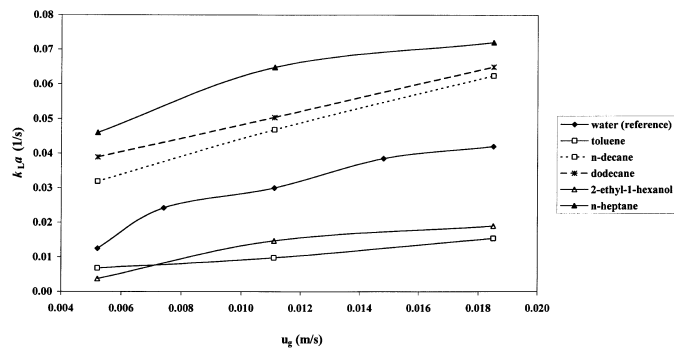


Figure 8. Mass transfer characteristics in terms of $k_L a$ in air–water and air–water–oil systems ($\phi_{disp} = 0.01$).

Nevertheless in this work it does not explain the mass transfer enhancement on its own, as the spreading coefficient of toluene is positive (+8.7 mN/m; data from McMillan and Wang, 1990), while this liquid does not increase the air–water mass transfer rate. The opposite result is also obtained for the case of dodecane, enhancing mass transfer and having a negative spreading coefficient (−2.7 mN/m from McMillan and Wang, 1990).

Figure 9 plots $k_L a$ versus ϕ_{disp} . The observed trend is very similar to that of the plot of enhancement factor versus ϕ_{disp} (Figure 6) which was based on initial flux and then is probably less precise than the determination of $k_L a$ obtained from the whole concentration recording. As in Figure 6, the highly non-linear effect of ϕ_{disp} is to be noticed. It could be due to the formation of an oil–water complex (several small water droplets entrapped in one large oil drop defined as multiple water droplets by Sajjadi et al., 2002), which would appear at higher concentration of dispersed phase and low gas velocity.

Conclusion

Mass transfer enhancement in gas–liquid system adding different second immiscible organic phases at low concentration has been measured and discussed. The overall gas hold-up is also measured. The volumetric mass transfer coefficient ($k_L a$) has been calculated by means of the dynamic method. Addition of 1% of some organic liquids (*n*-decane, dodecane and *n*-heptane) enhance gas–liquid mass transfer up to fourfold, whereas toluene, anisole and 2-ethyl-1-hexanol hinder mass transfer compared to air–water system. Addition of decyl alcohol increases mass transfer at moderate gas flow rate, but the rate of increase of mass transfer is less compared to the addition of *n*-decane, dodecane and *n*-heptane. However, the moderate changes in gas–oil saturated water interfacial properties due to oil addition do not explain these results. The remarkable effect of these very insoluble oils, much higher than predicted by shuttle effect theories, is then due to unexplained droplet interactions with the gas–liquid interface.

Future studies emphasizing interfacial properties, as well as the dynamic surface tension of organic liquids added to water, as in this three-phase medium and on measurements of the bubble size and drop size in gas–liquid–liquid system are to be performed to explain these phenomena in a more precise way.

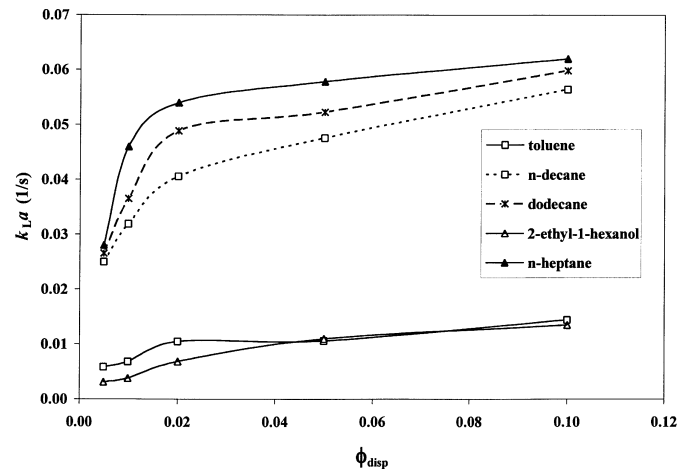


Figure 9. Effect of oil concentration on $k_L a$ in air–water–oil systems ($u_g = 0.0052$ m/s).

Nomenclature

a	interfacial area, (m^2/m^3)
C_G	concentration of oxygen in gas phase, (mol/m^3)
C_O	concentration of oxygen in dispersed liquid phase, (mol/m^3)
C_W	equilibrium concentration of oxygen between water and absorbed gas phase, (mol/m^3)
C_W	concentration of oxygen in water, (mol/m^3)
H	Henri constant, ($\text{Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$)
k_L	liquid side mass transfer coefficient, (m/s)
$k_L a$	volumetric mass transfer coefficient, (s^{-1})
m_R	solubility ratio
N	oxygen flux, ($\text{mol}\cdot\text{s}^{-1}$)
p	partial pressure of oxygen, (Pa)
P	total pressure, (Pa)
t	time, (s)
u_g	superficial gas velocity, (m/s)
V_G	volume of gas, (m^3)
V_L	volume of liquid, (m^3)
X	mole fraction

Greek Symbols

ε	gas hold-up
$\sigma^*_{\text{water air}}$	interfacial tension between air and water saturated with oil, (N/m)
ϕ_{disp}	dispersed liquid phase ratio

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