Review

Mass transfer enhancement of gas absorption in oil-in-water systems: a review

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Abstract

A review is presented on the gas–liquid mass transfer enhancement due to the presence of a second dispersed liquid phase. An attempt has been made to describe the mass transfer characteristics in a gas–liquid–liquid system. The ability of an immiscible oil phase to influence the possible pathway for gas transfer from the gas phase to the aqueous phase and to affect the gas–liquid interface and the volumetric mass transfer coefficient \( k_{La} \) is considered. Though the mass transfer in series looks the most logical explanation, there are many gaps and contradictions in the reported results of \( k_{La} \), preventing any definite conclusion being reached. An enhancement factor \( (E) \), which quantifies the effect of the oil addition on the gas–liquid mass transfer, is defined. Experimental enhancement factors are reported and compared to the theoretical maximum attainable enhancement factor \( (E_{\text{max}}) \). Possible mechanisms (“bubble co-covering”, “shuttle effect” and “permeability effect”) involved in mass transfer enhancement are assessed in detail. The commonly used “shuttle effect” mechanism, whose model proposes a direct usable expression of the enhancement factor, underestimates the reported experimental enhancement factors by about 20%. However, to date, it is not possible to satisfactorily propose a unique theory explaining the influence of the presence of an immiscible oil on mass transfer enhancement. Moreover, the development of sophisticated models has not yet reached satisfactory levels. Recommendations have been made for future research.

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1. Introduction

Reactions involving three-phase systems are frequently encountered in the chemical process industry. In general, the third phase (solid or liquid) dispersed in a gas–liquid system may be either a reagent, substrate or a heterogeneous catalyst. Although the majority of works are devoted to the gas–liquid–solid reactions [1], gas–liquid–liquid reactions are gaining importance due to the increase of this type of application in the bioprocess industry and homogeneous catalysis systems. In gas–liquid mass transfer, a very interesting situation may occur in the presence of small solid particles or when the second liquid is finely emulsified in the continuous liquid phase and the gas solubility in this dispersed liquid phase is higher than that in the continuous phase (solubility ratio \( m_g > 1 \)). In such cases, the presence of either solid particles or dispersed liquid droplets can significantly enhance the transfer rate of gas reactant into the continuous liquid phase. The aim in this paper is to analyse works devoted to gas–liquid–liquid systems. For a detailed review about gas–liquid–solid systems the reader is referred to Refs. [1,2]. Considering the work carried out during the past 30 years, experimental investigations and their modelling with the mass transfer enhancement in gas–liquid–liquid systems were discussed in the following areas: absorption with and without chemical reactions, mass transfer in biological systems and catalytic systems.

The present work was undertaken in order to sum up the investigations dealing with the mass transfer enhancement in restricted “oil-in-water” systems in the presence of gas (the term “oil” is used to represent the organic dispersed liquid phase and the term “water” represents the continuous aqueous liquid phase). This
The mass transfer enhancement in gas–liquid–liquid systems is defined with respect to the absorption rate in gas–liquid systems. In two-phase gas–liquid systems, there is an interface with concentration gradients on both sides (Fig. 1). Taking the case of a gas mixture of A and B with a non-volatile liquid which absorbs only A, there are three resistances to the transport of species A from gas phase to liquid phase: in the gas phase, at the gas–liquid interface and in the liquid phase. The mole fraction in the bulk gas phase is \( y_A \), which decreases to \( y_{AI} \) at the interface. In the liquid phase the mole fraction starts at \( x_{AI} \) and falls to \( x_A \). The interface resistance can be neglected in most operations except in very high flux cases. It is assumed that the concentrations at the interface are at steady state. The mole fractions \( y_{AI} \) and \( x_{AI} \) are then assumed to be in thermodynamic equilibrium. The fluxes of species A are written as:

\[
\text{gasphase:} N_A = k_G d (y_A - y_{AI}) \rho_G V \tag{1}
\]

\[
\text{liquidphase:} N_A = k_L d (x_{AI} - x_A) \rho_L V \tag{2}
\]

where \( k_L \) and \( k_G \) are the local mass transfer coefficients of the liquid phase and gas phase respectively, \( a \) is the specific interfacial gas–liquid area, \( \rho_G \) and \( \rho_L \) are the molar densities of the phases, \( V \) is the volume of the reactor and the differences in mole fractions represent the driving forces in each phase. Local mass transfer coefficients \( k_L \) and \( k_G \) can be linked to many theories such as the film, penetration and surface-renewal theories. The film theory assumes mass transfer by only molecular diffusion (\( D \)) within a film of thickness (\( \delta \)) depending upon the nature of the flow conditions. In this case, \( k \) (transfer coefficient) is given by Eq. (3). The penetration theory emphasises that the time of exposure of a fluid to mass transfer is short in many situations, so the steady state concentration gradient which is considered in the film theory cannot be assumed. The mass transfer is pictured as molecular diffusion in unsteady-state conditions at the boundary of the fluid, where \( t_L \) is the time of contact between gas and liquid. In this case, the local mass transfer coefficient is given by Eq. (4). Surface-renewal theory extends the penetration theory and assumes that the time of contact is not constant but a statistical function. The gas–liquid interface is then a mosaic of surface elements of different exposure times. Hence, a mean surface renewal factor, \( s = 1/t \) is introduced, where \( t \) is the average residence time at the interface. In this case, \( k \) is given by Eq. (5).

\[
\text{Filmtheory:} k = D/\delta \tag{3}
\]

\[
\text{Penetrationtheory:} k = 2(D/\pi t_L)^{0.5} \tag{4}
\]

\[
\text{Surface-renewaltheory:} k = (sD)^{0.5} \tag{5}
\]

The mass flux depends on the interfacial area \( a \) which is given by the following relation:

\[
a = 6e/d_b \tag{6}
\]

where \( e \) is the gas hold-up and \( d_b \) the bubble diameter.

When a third phase (a dispersed liquid phase) is added to a gas–liquid mixture, the system becomes more heterogeneous and complex. Consequently, one should be cautious when applying theories derived for two-phase systems to the gas–liquid–liquid three-phase systems.

2. Observations in gas–liquid–liquid systems

The aim of the addition of an organic phase which has a high affinity to the solute gas is to increase the mass transfer from the gas phase to the liquid phase. This is obtained mainly due to increased overall gas solubility in the mixture. In order to characterise the change in the specific gas absorption rate due to the presence of the organic phase, most investigations used the term “enhancement”. Because the objectives of their works were different, investigators have not selected uniform definitions, especially for “enhancement”, depending on whether they have included the solubility effect or not. There are two main objectives in their experiments: (1) investigations in which emulsion was achieved so as to promote gas absorption deliberately, in direct comparison with the purely physical absorption of the gas. Such investigations are important especially for bioprocesses where the oxygen uptake rate is very often the limiting rate. In this case, investigators obtained a maximum

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**Fig. 1.** Concentration profiles of solute A in the neighbourhood of a gas–liquid interfaces.
mass transfer enhancement by the use of an organic phase with high affinity for the solute gas; (2) investigations in which only the influence of the oil addition on the volumetric coefficient \( k_{L0} \) is considered. In this case, the potential enhancement due to the high solubility of the solute gas in the oil phase is taken into account to calculate \( k_{L0} \). Reported experimental results in the literature show that the \( k_{L0} \) value can decrease, remain unaffected or increase upon addition of a second, liquid phase having a higher solubility for the component to be transferred. So one must be very careful in comparing reported “enhancement” values proposed in the literature.

Most experiments described in the literature were carried out using a hydrocarbon or a perfluorocarbon (PFC) as dispersed phase in a stirred tank reactor, in a bubble column reactor and a stirred cell, a model reactor with a known constant interfacial area (which avoids effects that could be caused by change in interfacial area). Table 1 presents the investigations on gas–liquid–liquid systems in which the specific absorption rate was considered and in which the interfacial area was well defined. Table 2 summarises the investigations in which the interfacial area was not known, i.e. studies in which possible effects on the interfacial area are included. In both these tables, experimental investigations are further classified according to the type of absorption (absorption with reaction, physical absorption, absorption in the presence of micro-organisms), and, for each type of absorption, the investigations are classified according to the phase (liquid or gas) in which experimental parameters were measured in order to determine either the mass transfer enhancement \( (E) \) or the variation in \( k_{L0} \).

In the latter case, some investigators have separated the effect of oil addition on the interfacial area, \( \alpha \), from that on the liquid side mass transfer coefficient, \( k_L \) (Tables 1 and 2).

### 3. Parameters affected in the presence of the dispersed liquid phase

The addition of the dispersed liquid phase changes the rate of transfer of the solute gas across the boundary layer. Physical properties (density, viscosity, gas solubility and gas diffusivity) of the liquid mixture are changed and the gas–liquid characteristics (droplet distribution inside the boundary layer, possible pathways for mass transfer, mass transfer coefficient and gas–liquid interfacial area) can be changed due to the interfacial properties of the dispersed liquid. There have been three distinct approaches reported in the literature to explain the change in mass transfer in a gas–liquid–liquid system:

1. direct gas–liquid (dispersed phase) contact forming a ‘gas–organic complex’,
2. the shuttle effect of droplets carrying gas solute from the gas–liquid interface to the liquid bulk,
3. the dynamic interaction of the oil droplets with the concentration boundary layer causing increased turbulence or mixing in this layer.

In order to understand the mechanisms governing the mass transfer in three-phase systems, the distribution of organic and water phases near the gas–liquid interface has been estimated using various possible pathways for mass transfer.

#### 3.1. Mass transfer in the boundary layer: possible pathways

Basically two possible pathways exist:

Transfer in series: there is a gas \( \rightarrow \) water mass transfer into the liquid and no direct gas \( \rightarrow \) oil contact is possible (Fig. 2A, B).

Transfer in parallel: gas \( \rightarrow \) oil contact is possible and the gas \( \rightarrow \) water mass transfer as well as the gas \( \rightarrow \) oil mass transfer occur (Fig. 3).

Before presenting the reported results from the literature, it is necessary to note that some investigations have highlighted the importance of the interfacial properties of the three-phase systems on these possible pathways [3–9]. Indeed, according to these authors, the interfacial properties of the oil–water system expressed through the notion of the spreading coefficient \( (S) \) could have a strong influence on the pathways for mass transfer (i.e. on the variation in the interfacial area and the mass transfer coefficient). Although it was concluded that the spreading behaviour of oil could determine the mass transfer characteristics from solute gas to water in a given “oil-in-water” system, it appears clear that it is not possible to explain the oil distribution near the gas–liquid interface through this parameter only. The spreading coefficient, \( S \), of oil on water is defined as:

\[
S_{OW} = \sigma_{WG} - (\sigma_{DG} + \sigma_{OW}) \tag{7}
\]

where \( \sigma_{ij} \) is the surface tension between phase i and phase j. As defined by Eq. (7), \( S \) quantifies the ability of an oil phase to either bead up (form a droplet) or spread out (form a film) when contacting an aqueous phase. Oils with negative spreading coefficient \( (S < 0) \) tend to form discrete droplets, whereas those with a positive spreading coefficient \( (S > 0) \) tend to spread as a thin film over the bubbles. Ref. [10] has defined spreading coefficient in terms of initial value (with the value of pure component surface tension) and mutually saturated value \( (S_{OW}^0) \) for oil–water system. According to Ref.
Table 1
Experimental investigations devoted to gas absorption in “oil-in-water” systems with known interfacial area (flat gas–liquid–interface)

<table>
<thead>
<tr>
<th>Authors</th>
<th>Apparatus</th>
<th>Operating conditions</th>
<th>Measured parameter</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Absorption with chemical reaction</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mehra and Sharma [31]</td>
<td>Stirred cell, $d_{a} = 9.2$ cm; $V = 0.2$ l, $N_{s} = 60–120$ rpm, GL interface = $59.8 \times 10^{-4}$ m$^2$</td>
<td>$T$ (°C)</td>
<td>$S$ (mN m$^{-1}$)</td>
<td>$\phi_{disp}$ (–)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27</td>
<td>$H_{2}SO_{4}$</td>
<td>Chloro-benzene:</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Butene-1</td>
</tr>
<tr>
<td>Mehra and Sharma [32]</td>
<td>Stirred cell; $N_{s} = 60$ rpm, $d_{a} = 9.2$ cm; $V = 0.1$ l, GL interface = $59.8 \times 10^{-4}$ m$^2$</td>
<td>4.513 except: $\phi_{disp} = 0.01$; $d_{d} = 10–100$ nm</td>
<td></td>
<td>Butene-1</td>
</tr>
<tr>
<td>Mehra et al. [33]</td>
<td>Id. [31]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chaudhuri and Sharma [34]</td>
<td>Glass stirred cell, $d_{a} = 9.5$ cm; $V = 0.25$ l, $N_{s} = 1.33$ s$^{-1}$, GL interface = $59.8 \times 10^{-4}$ m$^2$</td>
<td>30</td>
<td>Aqueous alkaline solutions</td>
<td>Toluene</td>
</tr>
<tr>
<td>Bruining et al. [12]</td>
<td>Stirred cell contactor (four baffles), $d_{a} = 6.1$ cm; $V = 0.1$ l; $d_{s} = 35$ mm, $N_{s} = 440$ rpm</td>
<td>26</td>
<td>$Na_{2}SO_{3}$</td>
<td>Hexadecane:</td>
</tr>
<tr>
<td>Van Ede et al. [9]</td>
<td>Stirred cell; $N_{s} = 0–5s^{-1}$, $d_{a} = 12.82$ cm; $V = 1.65$ l, GL interface: $1.2321 \times 10^{-4}$ m$^2$</td>
<td>30</td>
<td>$Na_{2}SO_{3}$</td>
<td>Toluene</td>
</tr>
<tr>
<td><strong>Physical absorption</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**
- $d_{a}$: Diameter of the apparatus
- $V$: Volume of the apparatus
- $N_{s}$: Stirring speed
- $d_{d}$: Diameter of the dispersed phase
- $S$: Surface tension
- $\phi_{disp}$: Dispersion number
- $m_{R}$: Rate of mass transfer
- $E$: Efficiency factor
- $Q$: Flow rate of gas
- $Q_{inlet}$: Flow rate of gas at the inlet
- $Q_{outlet}$: Flow rate of gas at the outlet
Table 2  
Experimental investigations devoted to gas absorption in “oil-in-water” systems with unknown interfacial area

<table>
<thead>
<tr>
<th>Authors</th>
<th>Apparatus</th>
<th>Operating conditions</th>
<th>Measured parameters</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Absorption with chemical reaction</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sharma and Manhelkar [23]</td>
<td>Bubble columns, ( d_l = 6.6 \text{ cm} )</td>
<td>( T = 30 \text{ °C} ), ( W = 2.57 \text{ l} ), ( d_i = 60 \text{ mm} ); ( N_s = 200 - 650 \text{ rpm} )</td>
<td>( \phi_\text{abs} ) (-) ( \phi_\text{diss} ) (-) ( d_1 ) (µm) ( \phi_\text{m} ) (-) ( E ) factor (-)</td>
<td>Liquid ( k_L )</td>
</tr>
<tr>
<td>Mehta and Sharma [24]</td>
<td>Agitated contactor (four baffles); ( V = 1.51 \text{ l} ), ( d_i = 12.5 \text{ cm} ); ( d_l = 5.8 \text{ cm} ), six straight-blade disk turbine impeller; ( N_s = 750 \text{ rpm} )</td>
<td></td>
<td>( \phi_\text{abs} ) ( \phi_\text{diss} ) ( d_1 ) (µm) ( \phi_\text{m} ) (-) ( E ) factor (-)</td>
<td></td>
</tr>
<tr>
<td>Das et al. [28]</td>
<td>Stirred vessel (four baffles); ( d_l = 13.5 \text{ cm} ), ( V = 1.51 \text{ l} ), six bladed Rushton type; ( N_s = 1300 \text{ rpm} )</td>
<td></td>
<td>( \phi_\text{abs} ) ( \phi_\text{diss} ) ( d_1 ) (µm) ( \phi_\text{m} ) (-) ( E ) factor (-)</td>
<td></td>
</tr>
<tr>
<td>Linek and Benes [4]</td>
<td>Agitated vessel (four baffles); ( d_i = 67 \text{ mm} ), ( V = 0.858 \text{ l} ), seven four-blade impellers, mounted on the stirrer shaft; ( N_s = 15.8 \text{ s}^{-1} )</td>
<td></td>
<td>( \phi_\text{abs} ) ( \phi_\text{diss} ) ( d_1 ) (µm) ( \phi_\text{m} ) (-) ( E ) factor (-)</td>
<td></td>
</tr>
<tr>
<td>Cents et al. [25]</td>
<td>Agitated reactor (6-bladed Rushton turbine; four baffles); ( V = 2.5 \text{ l} ); ( d_i = 149 \text{ mm} ), ( d_l = 50 \text{ mm} ); ( N_s = 1100 \text{ rpm} )</td>
<td></td>
<td>( \phi_\text{abs} ) ( \phi_\text{diss} ) ( d_1 ) (µm) ( \phi_\text{m} ) (-) ( E ) factor (-)</td>
<td></td>
</tr>
<tr>
<td><strong>Physical absorption</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yoshida et al. [3]</td>
<td>Agitated vessel (four baffles); ( d_i = 15 \text{ cm} ), ( V = 2.57 \text{ l} ), ( d_i = 60 \text{ mm} ); ( N_s = 200 - 650 \text{ rpm} )</td>
<td></td>
<td>( \phi_\text{abs} ) ( \phi_\text{diss} ) ( d_1 ) (µm) ( \phi_\text{m} ) (-) ( E ) factor (-)</td>
<td></td>
</tr>
<tr>
<td>Hassan and Robinson [5]</td>
<td>Bubble column, ( d_i = 10 \text{ cm} ), ( h = 1 \text{ m} )</td>
<td></td>
<td>( \phi_\text{abs} ) ( \phi_\text{diss} ) ( d_1 ) (µm) ( \phi_\text{m} ) (-) ( E ) factor (-)</td>
<td></td>
</tr>
<tr>
<td>Lekhal et al. [29], Lekhal [30]</td>
<td>Stirred autoclave; ( V = 0.6 \text{ l} ), ( N_s = 0 - 2500 \text{ rpm} )</td>
<td></td>
<td>( \phi_\text{abs} ) ( \phi_\text{diss} ) ( d_1 ) (µm) ( \phi_\text{m} ) (-) ( E ) factor (-)</td>
<td></td>
</tr>
<tr>
<td><strong>Physical absorption in biological systems (in the presence of micro-organisms)</strong></td>
<td></td>
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</tr>
<tr>
<td>MacMillan and Wang [8,16]</td>
<td>Fermentation vessels; ( V = 1.25 \text{ l} ), ( N_s = 500 \text{ rpm} ), ( V = 11.5 \text{ l} ), ( N_s = 800 \text{ rpm} )</td>
<td></td>
<td>( \phi_\text{abs} ) ( \phi_\text{diss} ) ( d_1 ) (µm) ( \phi_\text{m} ) (-) ( E ) factor (-)</td>
<td></td>
</tr>
<tr>
<td>Junker et al. [18]</td>
<td>Fermentation vessel; ( V = 2.5 \text{ l} ), ( N_s = 800 \text{ rpm} )</td>
<td></td>
<td>( \phi_\text{abs} ) ( \phi_\text{diss} ) ( d_1 ) (µm) ( \phi_\text{m} ) (-) ( E ) factor (-)</td>
<td></td>
</tr>
<tr>
<td>Ju et al. [37]</td>
<td>Surface aerated bioreactors, ( N_s = 100 \text{ rpm} )</td>
<td></td>
<td>( \phi_\text{abs} ) ( \phi_\text{diss} ) ( d_1 ) (µm) ( \phi_\text{m} ) (-) ( E ) factor (-)</td>
<td></td>
</tr>
<tr>
<td>Van der Meer et al. [26]</td>
<td>Stirred tank reactor; ( N_s = 6.67 - 16.67 \text{ s}^{-1} )</td>
<td></td>
<td>( \phi_\text{abs} ) ( \phi_\text{diss} ) ( d_1 ) (µm) ( \phi_\text{m} ) (-) ( E ) factor (-)</td>
<td></td>
</tr>
<tr>
<td>Rols et al. [6]</td>
<td>Fermentation broth; ( V = 12 \text{ l} ), ( N_s = 400 \text{ rpm} )</td>
<td></td>
<td>( \phi_\text{abs} ) ( \phi_\text{diss} ) ( d_1 ) (µm) ( \phi_\text{m} ) (-) ( E ) factor (-)</td>
<td></td>
</tr>
</tbody>
</table>
[10], the spreading coefficient $S_{OW}$ is negative for nearly all systems and thus there is no spreading in these cases.

For beading oils, the most probable pathway is mass transfer in series. Only Ref. [5] has assumed a partial coverage of the bubble surface by the adhering beading oil droplets. When the spreading coefficient theory is not used, mass transfer in series has been adopted and represents a major assumption in the theoretical and modelling investigations. Models have been classified into “stationary” or “instationary” models and (pseudo)homogeneous or heterogeneous models [11]; Table 3). Basically, homogeneous models ignore geometric effects and concentration gradient inside the dispersed phase (Fig. 2A). Moreover, the fraction of the dispersed oil phase is assumed to be equally uniform in the gas–liquid interface and the liquid bulk. [12–15], assuming a “shuttle effect” of the oil phase, considered that the solute absorbed in the oil droplets near the gas–aqueous phase interface is given up to the water phase outside the boundary layer. The advantage of these homogeneous models is their numerical simplicity and short computation times [11]. In the heterogeneous models, the local geometry at the gas–liquid interface is taken into account (bubble–droplet distance and droplet–droplet distance are considered). For instance, Refs. [16,17] assumed two potential pathways across the gas–liquid interface (Fig. 2B): the solute gas is absorbed either by the continuous phase only ($N_{GW}$) or by the continuous phase followed by the dispersed phase ($N_{GWO}$). In the latter case, the transfer between droplets and aqueous phase takes place outside the boundary layer. It is to be noted that recent 3D models with spherical droplets, as presented by Ref. [11], are closer to reality than the one from Ref. [18]. Ref. [19] modified the approach of Ref. [18] by considering the same pathways and assuming that the transfer between droplets and aqueous phase could take place inside the boundary layer as well.

For spreading oils, the most probable pathway is the transfer in parallel, as investigated by Refs. [6,7]. Though Ref. [3] reported that direct gas → oil transfer is a significant pathway for oxygen absorption for spreading oils, Refs. [4,8] concluded that the mass transfer is in series even with $S > 0$ “oil-in-water” systems. Thus, it seems clear that mass transfer in parallel has only a marginal influence. However, Ref. [9] considered that mass transfer in parallel is possible whatever the interfacial property of the oil phase in “oil-in-water” systems. Ref. [10] has suggested the possible direct gas–oil contact through the formation of complexes of gas–organic drops which is dependent not only on the spreading coefficient but also on the bubble and droplet size. The probability of formation of these complexes has been expressed from the viewpoint of surface energy change where:

$$
\Delta E_s = 4\pi[(\sigma_{GO} R_b^2 + \sigma_{OW} R_c^2 - \sigma_{OW} R_d^2 - \sigma_{GW} R_b^2)]
$$

where $R_b$, $R_c$ and $R_d$ are the radius of the bubble, the complex and the droplet, respectively. The formation of a complex will be favourable for $\Delta E_s < 0$, from which

$$(R_b/R_d)^2 < \frac{\sigma_{OW}^2}{\sigma_{OW}^2 + \sigma_{OG}^2 - \sigma_{GW}^2} = -S_{OW}^2$$

($*\text{ refers to the situation in which both phases are at equilibrium with each other; “mutually saturated”}.$) The possibility of formation of organic complexes of gas–organic drops has also been reported by Ref. [20] due to the enhanced bubble–drop coalescence in these systems. But to go further through Brilman’s approach [11], we need the value of $S_{OW}$ which is not available in the literature and difficult to obtain. So further revalidation of his approach is required.

As stated earlier, it is not possible to explain the mass transfer phenomena due to the effect of addition of oil in a gas–liquid interface and boundary layer only by the spreading coefficient. Consequently, several investigations have been devoted to the variation in volumetric mass transfer coefficient $k_{1a}$ in these systems and this is in the following section.

3.2. Effect of oil addition on $k_{1a}$

$k_{1a}$ is usually used to characterise the gas absorption rate in multiphase reactors. Variations in $k_{1a}$ with addition of oil have been studied, taking into account and ignoring the spreading coefficient values of the “oil-in-water” system. In two-phase gas–liquid systems, some experimental methods are available to determine $k_{1a}$ [21,22]. In “oil-in-water” systems, the presence of the immiscible organic phase which has a high affinity for the solute gas must be taken into account in the determination of $k_{1a}$. Table 4 presents an overview of the methods used by the authors to experimentally determine $k_{1a}$. The various definitions of $k_{1a}$ in this table ignore liquid–liquid mass transfer limitation, i.e. an equilibrium of the dissolved gas between the aqueous continuous phase and the organic dispersed phase is assumed (Eq. (15)). Effects on the interfacial area $a$ and on the liquid side mass transfer coefficient $k_L$ are also analysed separately. Refs. [23–25] measured $k_L$ and $a$ simultaneously by chemical absorption. Ref. [4] first determined $k_{1a}$ from measurement of gas volume reduction due to absorption, then interfacial area $a$ from the bubble volume according to their shape.

Interfacial properties of the “oil-in-water” systems, particularly the spreading coefficient, have been used to explain some unusual variations in the mass transfer parameter $k_{1a}$ with the fraction of oil [3–5]. Strong effects at low dispersed organic phase fraction have been reported [25]. This could be consistent with the fact that the change in surface tension occurs at very low contents of the oil phase and does not play any role on further
addition of organic phase. Unfortunately, the influence of the spreading coefficient parameter (positive or negative) has not been systematically studied and contradictory reported results (Table 5; Fig. 4A, B) are presented. So it is not possible at this moment to explain the effect of interfacial properties of the dispersed phase on $k_L a$ and further investigation is required. For instance, Ref. [3] found that beading oils ($S < 0$) such as $n$-paraffin and kerosene impeded oxygen transfer (Fig. 4A) and concluded that a reduction in oxygen transfer resulted from decreased rates of oxygen diffusion through oil droplets partially occupying the liquid film. In contrast, Ref. [4] concluded that the reduction in $k_L a$ is caused by the decrease in the interfacial area $a$ rather than by decreased flux density. To further complicate the issue, Ref. [8] reported that this mechanism of flux reduction is likely to apply only to high viscosity oils, such as $n$-paraffin which have oxygen permeabilities below that of water, while Ref. [26] showed that $k_L a$ is unchanged in the presence of paraffin. However, the most contradictory results have been reported by Ref. [5]. These authors found that $k_L a$ for beading oils is increased with the increase in oil fraction ($n$-hexadecane) and decreased for $n$-dodecane up to a certain level of oil addition (Fig. 4A). However, they were not able to explain these opposing results.

In the case of positive spreading coefficient oils (oleic acid and toluene), Refs. [3,4] found that $k_L a$ exhibits an initial rapid decrease, followed by a gradual increase as oil loading is increased (Fig. 4B), though there is doubt about the extrapolation in the figure of [4] due to the presence of only three experimental data points in the smooth declining curve. This $k_L a$ change was attributed to opposing changes in both $k_L$ and $a$. According to these authors, oil that spreads over a gas–liquid interface increases the interfacial area $a$ at constant gas hold-up (by reducing the average bubble diameter), but decreases the mass transfer coefficient $k_L$ by increasing the liquid phase mass transfer resistance. A recent investigation carried out by Ref. [25] using toluene as a secondary organic phase confirmed the initial decrease in $k_L a$ previously reported by Ref. [3] even though they did not use the concept of spreading coefficient. According to Ref. [25], the initial decrease in $k_L a$ is completely due to a decrease in $a$, $k_L$ remaining practically constant. Unfortunately, these authors who observed a similar but lower decrease in $k_L a$ in the case

![Fig. 2. Mass transfer pathway in series: (A) example of pseudo-homogeneous model representation (no direct gas→oil contact; from Ref. [11]); (B) example of heterogeneous model representation (combination of flux to gas→water and gas→water→oil; from Ref. [18]).](image)

![Fig. 3. Mass transfer pathway in parallel.](image)
of addition of 1-octanol are not able to come to the same conclusion.

In the light of these controversial reported results, it seems that there are various interactions existing between gas bubble and oil droplets, so the only conclusion which can be drawn is that the interfacial properties of the "oil-in-water" system cannot be directly used to explain the peculiar trend of $k_L a$ with the fraction of oil. To provide a clear answer on the influence of the interfacial properties of the "oil-in-water" systems on $k_L a$ values (or on the possible pathways for mass-transfer), systematic investigations of the oil–water behaviour (with parameters other than spreading coefficient if necessary) should be carried out. However, quantitative studies of this problem are difficult.

3.3. Effect of oil addition on gas–liquid interfacial area $a$

The effects of the addition of any second liquid phase on the interfacial area appear to be very complex (Table 5). According to Ref. [24], the value of $a$ cannot be predicted a priori, as system properties have a profound effect on $a$. A marginal increase in $a$ was reported by Ref. [23] for bubble columns and by Ref. [24] for stirred vessels. These authors assumed that the presence of small droplets of organic phase could result in reduced rates of coalescence of gas bubbles and thus increased gas–liquid interfacial area. However, according to these authors, the influence of liquid droplets is not very significant. Ref. [6], measuring the bubble size by a photographic method, concluded that the bubble Sauter mean diameter was reduced by 15% and the gas–liquid interfacial area was increased proportionally. In contrast, Ref. [8], also using a photographic method to measure air bubble size distribution, found that $a$ did not vary with oil loading within the range 0–15%. Conversely, the drop size distribution became much wider with the introduction of gas bubbles, causing an increase in small-size drops, which may affect the mass transfer rate [27]. Ref. [28] observed that the presence of oil in gas–liquid dispersion in stirred vessels influences the interfacial area in a more complex way than previously reported. As the oil fraction is increased, the interfacial area expressed on the basis of a unit volume of dispersion or aqueous phase, first increases, passes through a maximum and then decreases. This trend was observed irrespectively of whether the area was determined by chemical or physical techniques. According to Ref. [28], the initial decrease in the average bubble diameter with increasing $\phi_{\text{disp}}$ would be due to the prevention of coalescence by the organic phase, while at higher $\phi_{\text{disp}}$ a diminished level in turbulence would prevent bubble breakage. Ref. [29], studying absorption dynamics of $\text{H}_2$ and CO into octene–water mixtures in a stirred autoclave (Table 2), observed the same trend in $k_L a$ versus the organic phase fraction as observed in the case of $a$ by Ref. [28], with a clear maximum at 3–4% of organic volume fraction (Fig. 5). They suggested that oil should not influence the gas-continuous phase mass transfer coefficient $k_L$ at low dispersed phase holdup and more probably the specific interfacial area is modified.

Obviously, one might imagine, once again, that the interfacial properties of the system could have something to do with the variations in mass transfer, but these contradictory results do not allow a coherent conclusion to be drawn. Further study is required to understand the variation of $a$ separately from $k_L a$ at low fraction of the dispersed phase.

3.4. Effect of oil addition on mass transfer coefficient ($k_L$)

The oil droplets might interact dynamically with the concentration boundary layer and thus increase the mass transfer coefficient $k_L$ by causing increased turbulence or mixing in the boundary layer. However, investigations into mass transfer enhancement due to hydrodynamic effects are difficult to carry out. Moreover, these effects involve numerous questionable assumptions (reduction of the contact time of the droplets inside the hydrodynamic boundary layer according to Eqs. (4) and (5), impingement of the bubble surface by droplets, turbulent instabilities in the vicinity of the boundary layer).

Ref. [23], studying the mass transfer coefficient in the presence of 2-ethyl hexanol in a bubble column, showed that the presence of the organic phase led to a decrease in $k_L$. According to these authors, it is likely that the small quantities of droplets decrease the interface mobility and produce a decreased mass transfer coefficient by interfering with the hydrodynamics of the system. More recently, Refs. [29,30] indicated that $k_L$ is not influenced by the presence of oil and Ref. [25] concluded that $k_L$ remains practically constant because it mainly depends on power dissipation and hydrodynamic conditions, which could be assumed constant in experiments.

The existence of hydrodynamic effects generated by oil droplets was suggested by Ref. [5]. They studied the effect of $n$-dodecane and $n$-hexadecane on the air-to-aqueous phase overall volumetric oxygen transfer coefficient in a simulated stirred-tank fermentor. The air-to-aqueous phase coefficients in both oil-free and oil-bearing systems were evaluated from unsteady-state experiments using a membrane-covered probe to follow the aqueous phase dissolved oxygen concentration. In order to explain the observed increase in $k_L a$ in the presence of $n$-hexadecane (Fig. 4A), these authors assumed the following mechanism: during the bubble residence time in the dispersion, its surface region is probably being bombarded with oil droplets. Some of
these droplets could approach the air–aqueous interface sufficiently closely by such mechanisms as direct interception or inertial impaction so that they become attached to the bubble. An air bubble with adhering oil droplets may then be circulated to a region where the turbulent shear forces are sufficiently large that the oil droplets would be dislodged from the bubble surface. The processes of droplet impingement on the bubble
surface and droplet removal by shearing forces are likely to result in localised disturbances of the aqueous volume elements at the interface, increasing the rate of mass transfer through increasing $k_L$. Obviously, this mechanism is open to criticism as, according to the authors, oil droplet diameter ranged from 2 to 20 µm, which implies low inertial effects. These effects should only be important in the case of large oil droplets with densities significantly higher or lower than that of water. Moreover, this hydrodynamic effect should lead to mass transfer enhancement in inverse “water-in-oil” systems and in “oil-in-water” systems with solubility ratio $m_R < 1$, which has never been reported in the literature.

Hydrodynamic effects are particularly difficult to study and no results show an increase in the mass transfer coefficient $k_L$ due to oil addition, so it seems clear that mass transfer enhancement in gas–liquid–liquid systems cannot be attributed to hydrodynamic considerations.

4. Mass transfer enhancement

4.1. Enhancement factor definition

To conclude this part, it appears that (1) even though the interfacial properties of the oil used seem to have some influence on the behaviour of the gas–liquid–liquid systems, the reported results in the literature are not able to give an accurate conclusion about this influence. The spreading coefficient, then, may be not the right parameter to use; (2) the mass transfer pathway for gas solute to the aqueous phase in gas–liquid–liquid system is possibly the mass transfer in series, as it is the more logical explanation and is used extensively in the literature; (3) the variation in the interfacial area with the addition of the oil is not explainable properly at this moment: increases and decreases in $a$ have been reported; and (4) the enhancement phenomenon cannot be attributed to an increase in $k_L$ linked to the oil addition.

Only in investigations where the objective is deliberately to promote the gas–liquid mass transfer, is the enhancement factor defined as the ratio of the absorption flux in the presence of third dispersed phase to that in its absence under the same hydrodynamic conditions and the same driving force for mass transfer:

$$E = \frac{N(\theta_{disp} \neq 0)}{N(\theta_{disp} = 0)} = \frac{J(\theta_{disp} \neq 0)A(\theta_{disp} \neq 0)}{J(\theta_{disp} = 0)A(\theta_{disp} = 0)}$$

where $J$ corresponds to the average flux density (mol m$^{-2}$ s$^{-1}$) through the gas–liquid interface and $A$ is the gas–liquid interfacial area (m$^2$). This definition assumes equilibrium at gas–continuous liquid interface and there is no direct contact between dispersed droplets and gas phase. Hence, the mass transfer pathway gas→contin-
uous liquid phase is favoured in order to conserve the same concentration driving force in three-phase as in two-phase systems. Experimentally, investigators used techniques in which the bulk concentration of the dissolved gas is negligible, which means that the driving force for mass transfer is well known. Negligible bulk concentration of the dissolved gas is obtained either by using chemical absorption methods [9,12,25,31–34] or by using biofermentors in which microorganisms are oxygen limited [8,16]. The enhancement factor definition also implies that the characteristic contact time (or the surface renewal frequency) at the gas–continuous liquid interface is not modified by the presence of the organic droplets. As mentioned above, k_L is not affected by the presence of the organic droplets, which means that this assumption is correct.

Fig. 6 presents some typical experimental results of the enhancement factor versus fraction of the dispersed phase. Though usually the enhancement factor E is within the range 1–4 (Table 1), enhancement factors up to 26 have been found experimentally [31,33]. However, only a few experimental enhancement results are available and comparison between the reported experimental enhancement factors is difficult, mainly due to the diversity of “oil-in-water” used, i.e. the diversity of the solubility ratio m_R (Table 1). These experimental enhancement factors can be compared with the theoretical maximum attainable enhancement factor.

4.2. Maximum attainable enhancement factor

According to Ref. [9], the theoretical maximum enhancement factor can be calculated by considering the transfer in the organic and the water phase to be completely in parallel, thus assuming direct gas–organic contact. Fig. 7 gives the transport rates to and from a small volume segment A_dx, according to the penetration model in the presence of chemical reaction. After balancing for the continuous part and the disperse part separately, the results are, respectively:

\[ D_W \frac{\partial^2 C_W}{\partial x^2} = \frac{\partial C_W}{\partial t} + k_e C_W^e \]  
\[ D_O \frac{\partial^2 C_O}{\partial x^2} = \frac{\partial C_O}{\partial t} \]  

(11)  
(12)

where D_W, C_W and D_O, C_O represent the diffusion coefficient and the concentration of the solute in the continuous phase (water) and in the oil phase, respectively. k_e C_W^e represents the chemical reaction term. In the slow reaction regime, Ref. [9] assumed that the mass transfer enhancement by the chemical reaction is negligible (see the part “shuttle effect”), thus the corresponding average fluxes through the gas–liquid interface are given by (penetration theory):

\[ J_W = 2[D_W/(\pi t_L)]^{0.5} C_W^e \]  
\[ J_O = 2[D_O/(\pi t_L)]^{0.5} C_O^e \]  

(13)  
(14)

Assuming liquid–liquid equilibrium of the solute:

\[ C_O^e = m_R C_W^e \]  

(15)

Eq. (14) can be rewritten as:

\[ J_O = 2[D_O/(\pi t_L)]^{0.5} m_R C_W^e \]  

(16)

Applying Eq. (10), Ref. [9] obtained the expression for the maximal enhancement factor:

\[ E_{\text{max}} = \frac{J_W(1 - \phi_{\text{disp}})A + J_O\phi_{\text{disp}}A}{J_W A} \]  

(17)

Using Eqs. (13), (16) and (17), the maximum enhancement factor by the penetration theory follows as:

\[ E_{\text{penetrationtheory}} = 1 + \phi_{\text{disp}}(m_R \sqrt{D_R} - 1) \]  

(18)

In this equation, D_R is the ratio of the diffusion coefficients (D_O/D_W).

For the film model (Fig. 7), Ref. [9] obtained in a similar way:

\[ E_{\text{filmtheory}} = 1 + \phi_{\text{disp}}(m_R D_R - 1) \]  

(19)

Eqs. (18) and (19) are identical for D_O = D_W only. According to Eqs. (18) and (19), the presence of a droplet phase (\phi_{\text{disp}} > 0, m_R > 1 and D_R ≈ 1) systematically leads to enhancement, E > 1 (Fig. 6). Fig. 6 and Eqs. (18) and (19) ideally represent the progressive replacement of the aqueous liquid phase by the oil. When comparing the experimentally observed enhancement factors (Fig. 6) with the maximum values as calculated by Eq. (18), it is logically confirmed that E is less than E_{\text{max}}. Fig. 8 shows the calculated difference (Eqs. (20) and (21)) existing between the reported experimental enhancement factors (E) and E_{\text{max}} calculated from the penetration theory (Eq. (18)).

\[ \text{Difference (\%) = } 100 \left( \frac{E - E_{\text{penetrationtheory}}}{E_{\text{penetrationtheory}}} \right) \]  
\[ i.e. \ \text{Difference (\%)} = 100 \left( \frac{E - (1 + \phi_{\text{disp}}(m_R \sqrt{D_R} - 1))}{1 + \phi_{\text{disp}}(m_R \sqrt{D_R} - 1)} \right) \]  

(20)  
(21)

The difference is equal to zero only if E reaches E_{\text{max}}. From Fig. 8, it is clear that mass transfer from the gas phase to both liquid phases does not occur in parallel, due to the presence of all experimental data points below the maximum attainable enhancement factor. Moreover, this transfer in parallel has scarcely been considered in the literature and only depicted (and called “bubble covering”) by Refs. [6,7].
4.3. “Bubble covering” mechanism

From a static visual study of gas–oil–water interactions with positive spreading coefficient oil (n-dodecane), Ref. [6] proposed that the main mechanism involved in the enhancement of the oxygen transfer rate is the layering of the oil as a thin film at the gas–liquid interface (Fig. 9). This mechanism requires a gas bubble–oil droplet coalescence (step 1) followed by an oil droplet–oil film coalescence (step 2). The coalescence phenomenon should result from the presence of hydrodynamic instabilities caused by bubble–droplet collisions, creating large waves in the liquid boundary layer. The basic idea of the model is that, when a bubble is submerged in the emulsion, the organic liquid covers the gas bubble surface possibly and the film formed is loaded with oxygen as long as the bubble has not exploded (Fig. 9, step 3). From the estimations of $k_L$ in the reactor, the main resistance should be located in the water film near the oil–water interface and thus, if the oxygen supply rate exceeds the oxygen demand rate in the aqueous phase, oil acts as an oxygen storage trap. Experimentally, Ref. [6] obtained increases in $k_L$ of 3.5 times with respect to a gas–water system with 40 µm oil droplet size and 5.4 times with respect to gas–water system with 1 µm oil droplet size (Fig. 10). From the physical description of the mechanism proposed, Ref. [7] developed a model which was not able to satisfactorily represent the experimentally observed decay in performances for high oil concentrations (Fig. 10). Considering this model, it appears that prediction of mass transfer enhancement by oil is difficult because of the lack of important information concerning interface properties, frequency of bubble–droplet collision, coalescence time, etc.

4.4. “Shuttle effect” mechanism

In contrast with the “bubble covering” mechanism, the “shuttle effect” has been extensively studied. The shuttle effect mechanism involves uptake of gas solute by the organic phase droplets in the diffusion film and a subsequent circulation of these “loaded” droplets through the gas solute deficient liquid bulk where it gives up the solute gas for reaction. The major assumption of this mechanism is that oil droplets are smaller than the film thickness. Consequently, they will be able to enter this highly concentrated layer and will provide a large liquid–liquid interfacial area [12,35]. This mechanism, first theoretically analysed using the steady state film theory by Ref. [31], was revalidated by Refs. [13,33]. They investigated the absorption of isobutylene, butene-1 and propylene in aqueous solutions of sulphuric acid.
in the presence of chlorobenzene as the dispersed phase (Table 1). A variety of physical situations, e.g. the case of reversible reaction of the diffusing solute with the droplets, were analysed using the penetration theory model as well as the surface renewal model. As the results are too extensive to be reported here, an example of the calculated enhancement factor (\(E\)) versus the solubility ratio (\(m_R\)) with droplet diffusivity as parameter (Fig. 11) is presented. For \(m_R\) ranging from 10 to 100, \(E\) ranged from 1 to 5, fitting roughly the enhancements cited in experimental works. In order to depict the “shuttle effect”, the study of Ref. [12] is presented here. Using the penetration theory, a model derived for the case where the distribution of the droplets in the emulsion is uniform with a first order reaction occurring only in the aqueous continuous phase has been proposed. As the chemical reaction leads to a mass transfer enhancement, this latter, depending on the hydrodynamic conditions and the reaction kinetics, is taken into account through the Hatta number:

\[
\text{Ha} = \frac{1}{k_L} \sqrt{\frac{2}{n + 1} k_1 D_W C_W^{n-1}}
\]

which is reduced to Eq. (23) in the case of a first order or a pseudo-first order reaction (\(n = 1\)):

\[
\text{Ha} = \sqrt{\frac{k_1 D_W}{k_L^2}}
\]

where \(k_1\) is the reaction constant, \(D_W\) is the diffusion coefficient of the solute gas in the continuous phase and \(k_L\) is the mass transfer coefficient. For slow reactions (\(Ha < 0.3\)), the mass transfer enhancement due to the chemical reaction is still unity. To validate the model, gas absorption experiments were conducted by Ref. [12] in a gas–liquid system in which oxygen was transferred from the gas phase to a sodium sulphite solution. Under the influence of cobalt ions as catalyst, sulphite reacts with dissolved oxygen to give sulphate. By varying the catalyst concentration, the reaction rate can be adjusted so that the bulk liquid concentration of oxygen is zero and the enhancement factor for mass transfer due to the chemical reaction is equal to one. When this condition is fulfilled, the concentration gradient from the gas–liquid interface to the liquid bulk is maximum. Under such conditions, a relatively large contribution from transport of a reactant by the freely moving droplets in the diffusional film to the total mass transfer is to be expected.

According to the penetration theory, the concentration gradient at the gas–liquid interface can be described by Eq. (24):

![Fig. 8. Calculated difference existing between the reported experimental enhancement factors (\(E\)) and, on the one hand, \(E_{\text{max}}\) calculated from the penetration theory (Eq. (21)) and, on the second hand, the modelling enhancement factor calculated from the “shuttle effect” (Eq. (28)). □: [9]; + : [12]; • : [16]; ● : [33].](image)

![Fig. 9. Sketch of “bubble covering” mechanism (from Refs. [6,7]).](image)

![Fig. 10. Effect of increasing concentrations of \(n\)-dodecane on \(k_{\text{la}}\) in a fermentation broth of \(A.\ aerogenes\) cells (from Ref. [6]). (1) Oil emulsified by ultrasonic treatment with pluronic F68 as surfactant. (2) Oil emulsified by mechanical agitation.](image)
the experimental enhancement factors being higher than predicted by Eq. (26) (see Fig. 6), it was concluded that the model was a useful first approximation of the observed phenomenon [12]. Fig. 8 shows the calculated difference (Eqs. (27) and (28)) existing between the few reported experimental enhancement factors and the modelling enhancement factor calculated from the “shuttle effect” (Eq. (26)).

\[
\text{Difference (\%)} = 100 \left( \frac{E - E_{\text{shuttle effect}}}{E_{\text{shuttle effect}}} \right)
\]

i.e. Difference (\%)

\[
= 100 \left( \frac{E - \sqrt{1 + \phi_{\text{disp}}(m_R - 1)}}{\sqrt{1 + \phi_{\text{disp}}(m_R - 1)}} \right)
\]

The difference is equal to zero only if \( E \) reaches \( E_{\text{shuttle effect}} \). From Fig. 8, it is clear that the “shuttle effect” model developed by Ref. [12] underestimates the actual mass transfer from the gas phase to both liquid phases. According to Ref. [12], the major assumption of the shuttle effect (this mechanism is valid provided that the droplets are smaller than the film thickness) should be verified. Moreover, investigations carried out with droplets larger than the film thickness did not show significant promotion of gas absorption [12]. Estimated from Eq. (3), the film thickness \( \delta \) is 23.5 \( \mu \)m which is higher than the droplet diameter \( (d_d = 10 \mu m) \) of the experiments by Ref. [12]. Furthermore, with such droplets, the time required for the “shuttle effect” to proceed would be short, the process being complete up to 99% at \( t = 0.125d_d/D_w \), i.e. \( 6.3 \times 10^{-3} \) s, which is fast relative to the surface renewal time: \( t_L = 0.35 \) s (using the penetration theory Eq. (4) with \( d_d = 10 \mu m, D_w = 2 \times 10^{-5} \) m s \(^{-1} \) and \( k_L = 8.5 \times 10^{-5} \) m s \(^{-1} \)). The major question about the significance of the shuttle mechanism is that experimental enhancements in the presence of droplets larger than the film thickness have been reported [6,16,18]. Obviously, experimental estimation of droplet diameter can always be open to criticism. Indeed, droplet diameters are distributed due to frequent coalescence and break-up. Ref. [27] confirmed the wide distribution of droplets size in gas–liquid–liquid systems. Then, the application of shuttle mechanism should not be limited by the droplet size.

According to Eq. (26), the addition (\( \phi_{\text{disp}} > 0 \)) of an organic oil with a high affinity for the solute gas (\( m_R > 1 \)) necessarily implies mass transfer enhancement. However, Ref. [25], assuming the concentration profile within the mass transfer zone is dependent on the oil used, suggested the existence of two types of gas–liquid–liquid system. For the first one, in the case of toluene and 1-octanol, the oil droplets are present in the mass transfer zone and it should be possible to apply Eq. (26); for the second one, in the case of \( n \)-dodecane and \( n \)-heptane, the oil droplets are not present in the mass transfer zone and no enhancement occurs. So restrictions of Eq. (26) should also be made. These results, which are in contradiction with the reported results by Ref. [6] at least for the \( n \)-dodecane (Fig. 10), should be further validated.

From the analysis of the “shuttle effect” previously reported, improved models have been proposed. A generalised pseudo-homogeneous model, accounting for the mass transfer rates between the two liquid phases and internal concentration gradient in the dispersed phase has been proposed by Ref. [15]. However, compared with the experimental data of Ref. [33], only a marginal improvement has been reported. The underestimation of mass transfer (Fig. 8) by homogeneous models could be due to their 1-D character which only considers the diffusion perpendicular to the gas–liquid [36]. Diffusion in other directions may also be very important. However, to take into account such con-
siderations, sophisticated models are required (as the 3-D heterogeneous model developed by Ref. [11]) involving information not available in the reported experimental works.

In conclusion, it can be said that the commonly used “shuttle effect” to depict mass transfer in “oil-in-water” systems underestimates the reported experimental enhancement factors (by about 20%). To explain mass transfer enhancement in a better way, some authors introduced the concept of the permeability of the solute gas, which is discussed in the following.

4.5. “Permeability effect”

Refs. [16,18] focussed their attention on the permeability effect which could also play an important role in mass transfer enhancement. While the importance of gas solubility in “oil-in-water” systems has been suggested by many researchers (using the solubility ratio \( \frac{m_R}{m_W} \)), the importance of gas diffusivity has been generally overlooked. According to Ref. [16], gas permeability, which takes into account both gas solubility and gas diffusivity, is a more accurate index of the capacity to transport solute than solubility alone. Indeed, in the case of high-viscosity oils, the effect of high gas solubility can be limited owing to low gas diffusivity. Using PFC FC40 as the dispersed phase, Refs. [16–18] investigated the oxygen absorption rate during fermentation. To predict the importance of permeability, models have been developed. Ref. [16] applied the surface renewal theory for diffusion into a immobile, heterogeneous liquid film whereas Ref. [17] used the penetration theory for the same. However, the two approaches are similar. These models can be regarded as a first approach to explaining mass transfer enhancement in systems where droplet diameters are larger than the film thickness \( \delta \). The model developed by Ref. [16] is discussed here. The indirect gas–oil contact geometry depicted in Fig. 12 has been considered. In this model, a thin layer of water of average thickness \( l_o \) exists at the gas–liquid interface separating the interface from the heterogeneous liquid dispersion. Hence oxygen first diffuses across the thin aqueous layer and then into either the oil dispersed phase or the continuous aqueous phase. To determine the total flux of gas across the gas–liquid interface, the contributions of the two potential pathways (gas–water and gas–water–oil) have been added together. The overall flux is thus given by:

\[
N = (1 - \varphi)N_{GW} + \varphi N_{GWO}
\]  

(29)

with \( \varphi \) representing the fraction of the specific gas–liquid interface area through which oxygen diffuses via the gas–water–oil path. The enhancement factor due to the permeability mechanism is given by the following expression (surface renewal model):

\[
E = 1 + 2\varphi \sum_{n=1}^{\infty} \frac{\varphi^n}{(D_O n)}^{1/2} \exp \left( -2n\sqrt{\frac{S}{D_O}} \right)
\]

(30)

with

\[
\varphi = \left( \frac{m_R D_O}{m_W D_W} \right)^{1/2} - 1
\]

(31)

The term \( \frac{m_R D_O}{m_W D_W} \) represents the permeability ratio between the oil and water phase. For uniform sized oil droplets, the model predicts a linear increase in the solute flux with an increasing oil volume fraction (Fig. 6). According to these authors, \( \frac{m_R D_O}{m_W D_W} \) and \( \frac{\varphi_{disp}}{\varphi} \) mainly determine the potential for mass transfer enhancement by the permeability effect. Ref. [17] indicated that oil acts as an oxygen sink, pulling oxygen through the water phase. The analysis proposed by Refs. [8,16] supported the conclusion that the aqueous phase is continuous at the gas liquid interface although the spreading coefficient of oil is positive (Table 2). Implicitly, the time scale for oil droplet–gas bubble interactions would be too short for the spreading of the oil droplet on the bubble to occur. Comparison of modelling and experimental results clearly indicates that the model fits the experimental data well at oil volume fractions below 0.3 (Fig. 6). Above oil volume fractions of 0.3, the model overestimates the enhancement. In addition to the square, regularly packed, droplets, which do not really represent the local geometry near the gas–liquid interface (Fig. 12), the main disadvantage of this model lies in the fact that Eq. (30) is not directly usable to all experimental results due to the unavailability of the parameter \( l_o \).

On the other hand, Ref. [37], investigating the capability of oil emulsions in enhancing oxygen transfer in bioreactors, proposed that the enhancement factor could be “directly” estimated from the product of ratios of oxygen permeability and solubility in media with and without emulsions. The predicted values of the enhancement factor were supported by the experimental results of \( k_{l,a} \) measurements and fermentations for systems with up to 15% oil. However, a further increase in oil volume fraction to 25% generally gave no further

![Fig. 12. Geometry of indirect gas–oil contact used for “permeability effect” modelling (from Ref. [16]).](image-url)
The major criticism of these models lies in the fact that parameters of the distribution of the dispersed phase near and inside the mass transfer zone are needed to accurately depict the mass transfer, but this information is lacking. In this case, models hold only for the conditions of the experimental system relevant to a particular study. Furthermore, only a few investigations compare the influence of the solubility ratio $m_R$, i.e. “shuttle effect” mechanism (Eq. (26)), and the influence of the diffusion ratio $D_R$ on the mass transfer enhancement. Considering $m_R$ and $D_R$ values reported by the literature (Fig. 6), the influence of diffusion ratio could only be significant for dispersed oil droplets having a low affinity for the solute gas. This moderate influence of $D_R$ on enhancement factor ($E$) is highlighted in Fig. 13 by heterogeneous models proposed by Refs. [36,38].

Though numerous approaches have been considered, it can be concluded that these mechanisms are difficult to describe, mainly due to the droplet distribution inside the boundary layer and the physical properties of the oil used. Moreover, these mechanisms are system specific with respect to the respective author’s study, which is why existing mechanisms have been further improved and new models have been proposed in order to correlate all experimental data.

4.6. Models

According to the literature, the heterogeneous models [9,16,17,19] have been over-simplified, as they assumed that the lateral transport between the droplets and adjacent liquid elements may be ignored. However, when droplet size is not much smaller than the liquid film thickness, the spherical effects become important, which will influence the composition gradient in the adjacent area. At the same time, the lateral transport near the droplets will become important [38]. Consequently, new models mainly taking into account the location and the interaction between droplets inside the boundary layer have been developed [11,36,38].

A numerical 1-D model, capable of handling multiple droplets and more complex situations has been presented by Ref. [36]. This model showed that the enhancement of gas–liquid mass transfer is dominated by the droplet closest to the interface.

To describe the mass transfer rate for “oil-in-water” systems containing droplets less than, equal to or larger than the liquid film thickness, Ref. [38] proposed an axisymmetrical heterogeneous mass transfer model based on the unsteady film-penetration theory. Droplet–droplet and droplet–film interactions were taken into account. To calculate the enhancement factor, the location ($\delta_1$) of the droplets in the gas–liquid boundary layer had to be given. Fig. 14 presents the variation in the estimated $E$ values versus the solubility ratio ($m_R$) with $\delta_1$ as parameter. For systems with a low solubility ratio ($m_R$), low enhancement factors were obtained. In such cases, droplets get easily saturated with the solute and do not contribute to the enhancement. It also appears that the enhancement factor increases with increasing $m_R$ before reaching a plateau; for very high $m_R$ values, $E$ is independent of $m_R$. This is consistent with the model proposed by Ref. [13] (Fig. 9).
As seen in Fig. 14, the location of the first droplet in the boundary layer ($\delta_1$) has an important effect on the enhancement factor ($E$). However, the location of the droplets can neither be predicted nor measured.

In their review devoted to mass transfer models in gas–liquid–liquid and gas–liquid–solid systems, Ref. [11] concluded that unsteady three dimensional mass transfer models are needed to investigate the importance of the geometrical factors involved in these systems. Effect of solute saturation of the droplet during the gas–liquid contact time must be taken into account. Ref. [11] developed a heterogeneous model in order to study the effect of droplets near the gas–liquid interface, droplet interaction also being included. The results obtained confirmed the prediction of the model proposed by Ref. [38]. The droplet–droplet interaction should be taken into account in the heterogeneous models in order to be able to describe the enhancement factors which have been shown to level off at higher dispersed phase hold-up [11]. However, detailed comparison is difficult since no accurate data on dispersed phase droplet size and distribution have been reported in the literature.

To conclude, it can be said that heterogeneous mass transfer models were developed in order to increase the level of understanding of the mass transfer enhancement phenomena at the gas–liquid interface. However, it is not sure that experimental results currently available could give accurate values of the parameters used in these models. Furthermore, although the heterogeneous models are to be preferred from a physical point of view, the homogeneous models are able to describe the experimental data equally well for simple cases while requiring less detailed parameter values and being computationally easier [25].

5. Conclusion

Information available on gas–liquid mass transfer in the presence of oil droplets has been reviewed critically. From this review, it appears that experimental investigations have led to large variations in the reported mass transfer enhancement results. Comparison between these results is difficult due to the variety of gas–oil–liquid systems used and the large number of relevant parameters. Furthermore, there is a sharp contrast between the large number of papers presenting models and the few papers which have presented experimental data in gas–liquid–liquid systems. To date, it is not possible to propose a unified theory to satisfactorily describe the influence of the presence of immiscible oil on mass transfer enhancement. There are many gaps in our knowledge, especially about the influence of oil addition on the mass transfer parameters $k_L$ and $a$. Physicochemical effects are often cited but never clearly worked out. The main conclusions are:

1) The mass transfer from the gas phase to both liquid phases may not occur in parallel. The mass transfer in series is a more logical explanation and is used extensively in the literature.

2) Even though the interfacial properties of the oil used seem to have some influence on the behaviour of the gas–liquid–liquid systems (especially at low dispersed phase fraction), the reported results in the literature are not able to lead to an accurate conclusion about this influence. Thus, the spreading coefficient may not be the right parameter to use.

3) There is no proper explanation for the variation in the interfacial area with the addition of oil at this moment: both increases and decreases in $a$ have been reported.

4) The enhancement phenomenon cannot be attributed to an increase in $k_L$ linked to the oil addition. A mechanism such as the “shuttle effect” must take first place.

5) Though enhancement factors up to 26 have been found experimentally, usually the enhancement factor $E$ is within the range 1–4.
6) The commonly used “shuttle effect” mechanism, as modelled by Ref. [12], underestimates the reported experimental enhancement factors (by about 20%) and should not be applied in the case where droplets are larger than the mass transfer zone. However, this mechanism is the only one to propose a direct usable expression for the enhancement factor.

7) The determinant parameters are $\phi_{\text{disp}}$ (fraction disperse phase), $m_R$ (solubility ratio) and $D_R$ (diffusivity ratio). Though the diffusivity ratio ($D_R$) has a lesser influence on enhancement factor ($E$) than the solubility ratio ($m_R$), it must be taken into account and could correct the gap existing between experimental enhancement factors and those modelled through “shuttle effect”.

8) In gas–liquid–liquid systems, mass transfer models are difficult to describe, mainly due to the droplet distribution inside the boundary layer and the physical properties of the oil used. Moreover, models hold only for the conditions of the experimental system relevant to a study. The main disadvantage of these models involves the use of parameters which can neither be predicted nor measured and insufficient input data have been reported in the experimental studies. Heterogeneous models are to be preferred from a physical point of view, but homogeneous models are able to describe the experimental data equally well for simple cases while requiring less detailed parameter values and being computationally easier.

Additional experimental research is necessary and both physicochemical and hydrodynamic approaches should be considered in more detail. It is clear that this issue is full of complexities and specially designed experiments will be needed, as follows:

1) The increase or decrease in volumetric mass transfer coefficient in gas–liquid–liquid system has been observed with very limited numbers of organic phases, in the literature. Consequently, there is a need for experiments with a number of organic phases to see the trend of mass transfer characteristics.

2) Systematic investigations into the influence of the interfacial properties of the “oil-in-water” systems on $k_{LI}$ variation (with parameters other than spreading coefficient if necessary) should be carried out. A clear answer about the influence of the interfacial properties especially at low dispersed phase fraction should be provided. The ability of an oil phase to affect the bubble breakup/coalescence phenomena also needs to be systematically investigated.

3) Experimental enhancement factors need to be measured in order to validate the models, i.e. to quantify the influence of solubility ratio ($m_R$) and diffusivity ratio ($D_R$). Comparison between experimental enhancement factors for different “oil-in-water” systems with same ($m_R$) values are required.

4) The existence of two types of gas–liquid–liquid systems, based on the ability of the oil to penetrate or not the mass transfer zone, need to be confirmed.

5) Information on the hydrodynamic characteristics (e.g. gas holdup, bubble size distribution) on the addition of an immiscible organic phase to a gas–aqueous liquid phase system is very rare and these need closer study. This will help to explain the mass transfer characteristics in gas–liquid–liquid systems in a better way. A study of drop size distribution is also required in actual systems like bubble column reactor and agitated vessel.

6) Lastly, there is still a lack of a unified model which can explain mass transfer enhancement in gas–liquid–liquid systems. Both mass transfer in series and in parallel may be considered for the modelling.

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Appendix A: Nomenclature

- $A$ interfacial active area (m$^2$)
- $a$ specific interfacial area between gas and liquid (m$^{-1}$)
- $C^*$ concentration at the gas liquid interface in equilibrium with partial pressure of solute in gas phase (mol m$^{-3}$)
- $C$ concentration of solute in liquid phase (mol m$^{-3}$)
- $C_{AL}$ aqueous phase equivalent of concentration of solute in oil phase (mol m$^{-3}$)
D  molecular diffusion coefficient of the solute (m² s⁻¹)

$d_\text{a}$ apparatus diameter (m)

$d_b$ bubble diameter (m)

$d_d$ droplet diameter (m)

$d_G$ Sauter mean bubble diameter (m)

$d_i$ impeller diameter (m)

$D_R$ diffusion ratio ($D_R = D_C/D_W$)

$E$ enhancement factor

$F$ feed rate (m³ s⁻¹)

$h$ height (m)

$H$ Henry’s law solubility constant (mol m⁻³ Pa⁻¹)

$k$ local mass transfer coefficient (m s⁻¹)

$k_1$ first order rate constant (s⁻¹)

$l_o$ thickness (m)

$M$ molar mass (kg mol⁻¹)

$m_R$ relative solubility ($m_R = (\text{solubility of solute in droplet phase})/(\text{solubility of solute in continuous phase})$)

$N_s$ rotational speed (s⁻¹)

$n$ reaction order

$N$ molar flux of A (mol s⁻¹)

$P^*$ pressure of gas in the bulk at saturation (Pa)

$P$ pressure of gas in the bulk (Pa)

$P_R$ permeability ratio

$R$ ideal gas constant (J mol⁻¹ K⁻¹)

$R$ radius (m)

$R_D$ thickness of continuous phase layer in the two phase gas–liquid boundary layer (m)

$s$ mean surface renewal factor (s⁻¹)

$S$ spreading coefficient (N m⁻¹)

$T$ temperature (K)

$t$ time (s)

$t_L$ contact time between gas and liquid in penetration theory (s)

$V$ volume (m³)

$x$ distance from gas–liquid interface (m)

$x_A$ mole fraction A in the liquid phase

$x_{AI}$ mole fraction A in liquid at the gas–liquid interface

$y_A$ mole fraction A in the gas phase

$y_{AI}$ mole fraction A in gas at the gas–liquid interface

Greek letters

$\rho$ molar density (mol m⁻³)

$\Omega$ surface (m²)

$\delta, \delta_f$ film thickness (m)

$\delta_I$ distance between interface and oil droplet in the boundary layer (m)

$\varepsilon$ gas holdup

$\phi_{\text{disp}}$ fraction dispersed phase

$\eta$ viscosity (Pa s⁻¹)

$\phi$ fraction of the specific gas–liquid interface area which solute diffuses via the gas–water–oil path

$\sigma$ interfacial tension (N m⁻¹)

$\Delta E_S$ surface energy change (N m⁻¹)

Subscripts

A component A

b bubble

c complex

d droplet

disp dispersed phase

eff effective

g gas

I interface

L liquid

o oil

W water

$\phi_{\text{disp}}$ fraction dispersed phase

References


