

MODELLING OF THE OVERALL VOLUMETRIC MASS TRANSFER COEFFICIENT MEASURED BY THE DYNAMIC METHOD IN GAS-LIQUID-LIQUID SYSTEMS

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ABSTRACT

Liquid-liquid emulsions encountered in aerobic bioprocesses consist of an immiscible dispersed oil phase that acts as a solute gas vector or the bioprocess substrate. Mass transfer of solute gases into such systems has been a topic of continual research. It has been established that the oil phase is responsible for the higher solubility of the solute gas, but its presence also affects the overall volumetric mass transfer coefficient. Enhanced, depressed and constant values of the latter have been reported in literature, and such varied behaviour has long posed a difficulty in its modelling. However, recent studies on the equivalent absorption concept have illustrated that varied behaviour of the overall volumetric mass transfer coefficient can be linked to how changes in the emulsion's solubility are accounted for in the formulations describing the system. These findings suggest that current reports in literature can be reconciled by reviewing how different formulations account for the emulsion's solubility.

This study re-examines formulations used to study mass transfer by the frequently employed dynamic method. The overall volumetric mass transfer coefficient, as measured by this method, is modelled in terms of modified enhancement factor models. These models are able to simulate enhanced, depressed and constant values of the overall volumetric mass transfer coefficient. Furthermore, the models are validated against two experimental case studies that considered oxygen absorption into perfluorocarbon/water and n-alkanes/water emulsions. It is concluded that these models can be used in future empirical and predictive studies on mass transfer by the dynamic method in gas-liquid-liquid and gas-liquid-liquid solid systems.

KEYWORDS

Gas-liquid-liquid; overall volumetric mass transfer coefficient; equivalent absorption concept; dynamic method.

NOMENCLATURE

C^*, C_w^*, C_o^* saturation concentration of the solute gas in the emulsion, aqueous and oil phases respectively (mol/m^3).
 C, C_w, C_o concentration of the solute gas in the emulsion, aqueous and oil phases respectively (mol/m^3).
 C_g concentration of the solute gas in the gas phase (mol/m^3).
 $K_L a'$ overall volumetric mass transfer coefficient as given by equation (1) (s^{-1}).

$K_L a$ overall volumetric mass transfer coefficient as given by equation (4) (s^{-1}).
 $K_L a_{x=0}$ overall volumetric mass transfer coefficient of pure water, (s^{-1}).
 x oil phase volume fraction.
 m solubility ratio (mol/m^3 oil phase / mol/m^3 aqueous phase).
 D_r diffusivity ratio (m^2/s oil phase / m^2/s aqueous phase).
 E enhancement factor.
 E' modified enhancement factor as given by equation (10).
 F gas feed rate (m^3/s).
 V total liquid volume (m^3).

Superscripts

in inlet.
out outlet.

INTRODUCTION

Mass transfer of a solute gas into liquid-liquid emulsions is a topic of interest with applications in industrial aerobic bioprocesses such as alkane bioconversions and biological waste gas treatment [1,2]. Liquid-liquid emulsions employed typically consist of a continuous aqueous phase and an immiscible dispersed oil phase such as hydrocarbons [1,2]. The aqueous phase supports the biological phase (organisms) but suffers from low solubility of the solute gas at normal process conditions [3] thus limiting the organisms' activities [2]. The oil phase, on the other hand, usually has a higher solubility of the solute gas. Thus, it may be added to the aqueous phase to act as a reservoir or vector of the solute gas [2-4]. Alternatively, as is the case in certain bioprocesses such as alkane bioconversions, the oil phase may itself be the bioprocess substrate [15].

Besides the enhanced solubility of liquid-liquid emulsions, the presence of the dispersed oil phase has been reported to affect the overall volumetric mass transfer coefficient in varied ways. The latter value, commonly measured by the dynamic method, has been reported to either increase, decrease or remain constant with increase in volume fraction of the oil phase [1,5]. Such variation has long posed a difficulty in the consistent modelling and comparison of results [2,6]. In addition, few studies have successfully reconciled their results to traditional enhancement factor models such as the shuttle effect [7,8].

Recently though, varied behaviour of the overall volumetric mass transfer coefficient has been linked to whether or not the enhanced solubility of the emulsion (expressed in terms of the equivalent absorption concept) is accounted for in the formulations describing the system [9,10]. In addition, these authors have suggested that a measured decrease of the overall volumetric mass transfer coefficient is actually an apparent decrease that occurs so as to balance the increase in the solubility (hence concentration driving force) of the emulsion [10]. These findings suggest that the varied behaviour of the overall volumetric mass transfer coefficient reported in literature can be reconciled by reviewing how different formulations account for the emulsion's enhanced solubility.

This study reviews formulations applicable to the commonly employed dynamic method. It is shown that values of the overall volumetric mass transfer coefficient, as measured by the dynamic method, can be modelled on the basis of modified enhancement factor models. The latter are based on traditional enhancement factor models while also accounting for solubility changes in the system. Two case studies have been provided to validate these models.

THEORY

Mass transfer of a solute gas into liquid-liquid emulsions is commonly studied by the dynamic method [11-15]. This is a physical method for measuring the overall volumetric mass transfer coefficient that involves the observation of changes in the liquid phase concentration of a solute gas in response to a step change in its partial pressure in the inlet gas. The observed non-steady concentration change profiles are then fitted to first order or second order model equations that respectively neglect or account for probe dynamics; and the overall volumetric mass transfer coefficient is computed from these model equations.

Equation (1) below is a first order model that suffices for the theoretical considerations herein:

$$\frac{dC}{dt} = K_L a' (C^* - C). \quad (1)$$

In equation (1), the emulsion's saturation concentration (C^*) is defined as the volumetric average of the saturation concentrations of the individual liquid phases [4,7,9] as given by equation (2) below:

$$C^* = (1 - x)C_o^* + xC_w^* = (1 - x + xm)C_w^*. \quad (2)$$

C_o^* and C_w^* in equation (2) are the saturation concentrations of the solute gas in the oil and aqueous phases respectively. x is the volume fraction of the oil phase and m is the solubility ratio that arises from the assumption of equilibrium between the aqueous phase and the dispersed oil phase that is expressed by equation (3) below:

$$C_o^* = mC_w^*. \quad (3)$$

C and $K_L a'$ in equation (1) respectively represent the emulsion's solute gas concentration and the emulsion's overall volumetric mass transfer coefficient. The latter has been reported in literature to either increase, decrease, or remain

constant with increase in volume fraction of the oil phase [1,5] thus posing a difficulty in its modelling [2,6]. However, recent studies have illustrated that the observed varied behaviour should be linked to changes in the emulsion's solubility [9,10]. In particular, the authors considered the absorption of styrene gas into a silicone oil/water emulsion and suggested that an observed decrease in $K_L a'$ occurred so as to balance an increase in the emulsion's solubility, given that no enhancement was observed in the mass transfer rate of styrene [10].

Models for $K_L a'$ measured from the dynamic method and illustrating such a linkage to changes in solubility can in fact be derived. To do so, mass balance equations (equations (4) – (5)) for the solute gas are necessary as a starting point and these can be written out as [16]:

$$-\frac{dC_g}{dt} = E \cdot K_L a (C_w^* - C_w), \quad (4)$$

$$-\frac{dC_g}{dt} = (1 - x) \frac{dC_w}{dt} + x \frac{dC_o}{dt} = (1 - x + xm) \frac{dC_w}{dt}, \quad (5)$$

where $K_L a$ is a measure of the overall volumetric mass transfer coefficient (discussed later on) and E is an enhancement factor. C_g , C_o and C_w are the concentrations of the solute gas in the gas, oil and aqueous phases respectively and other terms are as previously defined.

Equation (4) accounts for possible mechanisms of mass transfer across the gas-emulsion interface as introduced by the enhancement factor (E). Two possible mechanisms were postulated by the original authors [16]; namely, series mass transfer without shuttling and parallel mass transfer. Later authors [17] have since then considered series mass transfer with shuttling [18]. The associated enhancement factors are respectively captured by equations (6) – (8) below:

$$E = 1, \quad (6)$$

$$E = 1 - x + xm\sqrt{D_r}, \quad (7)$$

$$E = \sqrt{1 - x + xm}, \quad (8)$$

where D_r in equation (7), which is based on the maximum enhancement factor by the penetration theory [19], is the ratio of diffusivity of the solute gas in the oil phase to that in the aqueous phase.

Equation (5), on the other hand, introduces the effect of the greater absorption capacity (solubility) of the emulsion. From the perspective of the aqueous phase, equation (5) dictates that the rate of change in solute gas' concentration in the aqueous phase of the emulsion ($x > 0$) will be slower than the equivalent rate of change in the case of pure water ($x = 0$). Alternatively, the rate of change in solute gas' concentration in the aqueous phase is equivalent to the rate of change in the gas phase scaled down by a solubility factor.

Combining equations (4) and (5), as the original authors [16] did, one obtains a fundamental model applicable to liquid phase analysis of the solute gas' concentration as given by equation (9) below:

$$\frac{dC_w}{dt} = E' \cdot K_L a (C_w^* - C_w), \quad (9)$$

where the modified enhancement factor (E') is defined as a scale down of the traditional models (equations (6) – (8)) by a solubility factor, that is:

$$E' = \frac{E}{1-x+xm} \quad (10)$$

A comparison of equations (1) and (9) illustrates that the former can be obtained from the latter by pre-multiplying both sides of equation (9) by the solubility factor (see equation (2)). More significantly, a definition for emulsion's overall volumetric mass transfer coefficient ($K_L a'$) emerges as equation (11) below:

$$K_L a' = E' \cdot K_L a \quad (11)$$

The $K_L a$ value, as posed in equations (4) – (8), has been previously measured and reported as constant and equal to the value in pure water ($K_L a_{x=0}$) for the absorption of oxygen into aqueous emulsions of n-alkanes (C₁₁-C₁₈) at oil phase volume fractions of up to about 20% [16]. Similar results have been reported for the absorption of oxygen into aqueous emulsions of dodecane and hexadecane for oil phase volume fractions up to 10% [20]. These findings permit equation (11) to be expressed as:

$$\frac{K_L a'}{K_L a_{x=0}} = E' \cdot \frac{K_L a}{K_L a_{x=0}} \approx E', \quad (12)$$

where the approximation in equation (12) is introduced since reports of varied behaviour of the $K_L a$ values also exist in literature. Such variance in $K_L a$ values has been attributed to changes in the interfacial area per unit volume [17], possible surfactant behaviour of the oil phase [16,21] and inversion of the emulsion from oil-in-water to water-in-oil at large oil phase volume fractions; $x > 20\%$ [16] and $x > 60\%$ [22].

The reporting of either $K_L a$ or $K_L a'$ values in literature depends on the formulations employed. A reporting of $K_L a$ can be traced to the use of equations (4) – (8) as the starting point [16,17,20,21,23]. However, the dynamic method is also frequently employed [11-15,24,25]. A need for consistent comparison between $K_L a'$, $K_L a$ and $K_L a_{x=0}$ values justifies the derivation of equations (10) – (12). A similar attempt has been previously made by Cesário, Beverloo et al. [24] as is illustrated in the Appendix.

CASE STUDIES

Two case studies that have reported $K_L a'$ values based on the dynamic method are assessed herein. It is initially assumed that the approximation of equation (12) holds and deviations from this are noted. Modified enhancement factors employed in equation (12) are based on traditional models of mass transfer such as series with and without shuttling [16-18], represented by equations (13) and (14) respectively. In addition, equation (15) represents the modified enhancement factor for parallel mass transfer [19]. Variants of this latter equation have been proposed in literature [26,27]. Figures 1 and 2 respectively show how equations (13) and (15) vary with oil phase volume fractions for different solubility and diffusivity ratios. Equation (14) gives similar curves to equation (13) and hence is not included.

$$E' = \frac{1}{\sqrt{1-x+xm}}, \quad (13)$$

$$E' = \frac{1}{1-x+xm}, \quad (14)$$

$$E' = \frac{1-x+xm\sqrt{D_r}}{1-x+xm}. \quad (15)$$

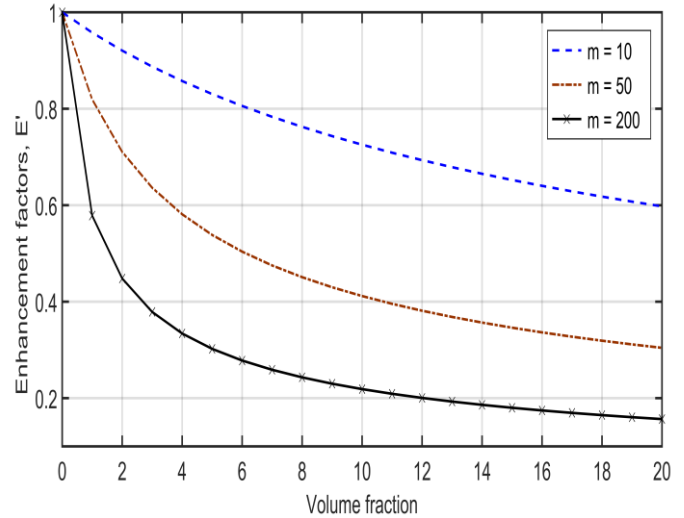


Figure 1: Modified enhancement factor for series mass transfer with the shuttle effect and solubility changes accounted for (equation 13).

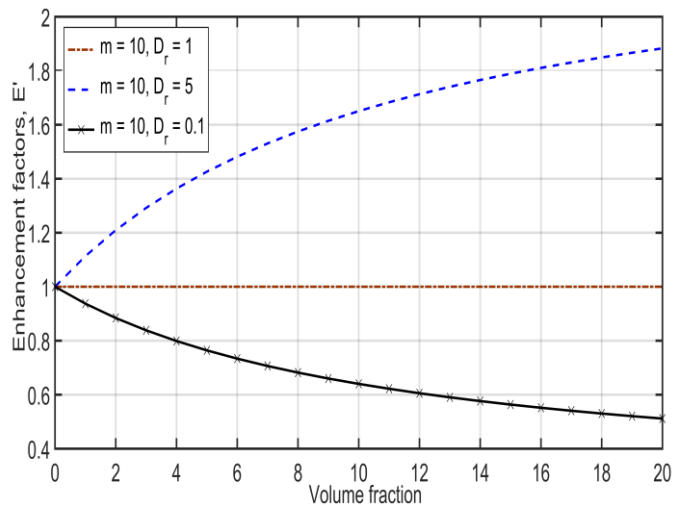


Figure 2: Modified enhancement factor for parallel mass transfer with solubility changes accounted for (equation 15).

Cesário, Beverloo et al. [24] examined the absorption of toluene and oxygen into a perfluorocarbon/water mixture in a stirred tank reactor. They obtained $K_L a'$ values that did not vary significantly. To explain this, the authors assumed that mass transfer would take place by the parallel pathway, given that perfluorocarbon has a positive spreading coefficient which implies that it (perfluorocarbon) would likely spread as a film on the air bubbles. Experimental enhancement factors have been computed from their reported $K_L a'$ and $K_L a_{x=0}$ values and are compared against predictions by equations (13) and (15) in Figure 3 for the poorly soluble gas case (oxygen). An assumed

10% interval is included in the results to account for experimental accuracy.

It can be observed from Figure 3 that both the modified parallel pathway model (equation (15)) and the modified shuttle effect model (equation (13)) give predictions that are within 10% of the experimental findings. Though both models predict a depression with increase in oil volume fraction, equation (13) predicts a steeper trend than equation (15). More experiments would be required at volume fractions greater than 10% to conclusively establish which of the two models is appropriate. This notwithstanding, it can be deduced (from Figure 3) that a positive spreading factor may be necessary but is not sufficient to indicate parallel mass transfer.

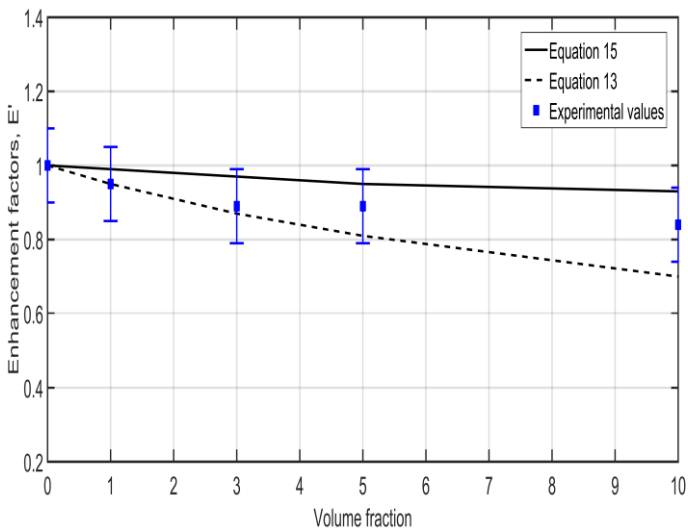


Figure 3: Experimental versus predicted enhancement factors for oxygen absorption into a perfluorocarbon/water emulsion with solubility ratio ($m = 11.7$) and diffusivity ratio ($D_r = 0.8$) [24].

Correia, Aldrich et al. [28] examined the absorption of oxygen into n-alkanes (C_{10} - C_{13})/water dispersions. Their $K_L a'$ values were determined by the pressure step method [29] and these have been recently re-measured using the dynamic method with the probe response accounted for [14]. Experimental enhancement factors have been computed from their reported $K_L a'$ and $K_L a_{x=0}$ values and are compared with equations (13) and (14) in Figure 4. An assumed 10% interval is included in the results to account for experimental accuracy.

It can be observed from Figure 4 that both models for series mass transfer (equations (13) and (14)) give predictions that are within 10% of experimental results. Agreement with equation (14) in particular reflects the findings of a previous study that looked at oxygen absorption into an aqueous emulsion of different n-alkanes – C_{11} - C_{18} [16]. However, in the latter study, individual bubbles rising through the turbulent emulsion were examined whereas the setup employed by Correia, Aldrich et al. [28] and Clarke & Manyuchi [14] allowed for secondary bubble coalescence and dispersion. This suggests that secondary coalescence and dispersion did not significantly alter the mass transfer mechanism in turbulent flow.

It is further observed from Figure 4 that there is some scatter of data at an oil phase volume fraction of 2.5% that

affects both datasets employed [14,28]. Though this could be dismissed as experimental error, recent studies on oxygen absorption into dodecane/water and hexadecane/water emulsions have suggested that the $K_L a$ value increases to a maximum at low volume fractions ($0\% < x < 5\%$) and decreases thereafter [21,22]. $K_L a$ peaks have also been observed at low volume fractions ($3\% < x < 4\%$) for the absorption of hydrogen and carbon monoxide into an octene/water emulsion [17]. Though varied reasons have been suggested for the $K_L a$ peaks, further experimentation is required at these low volume fractions.

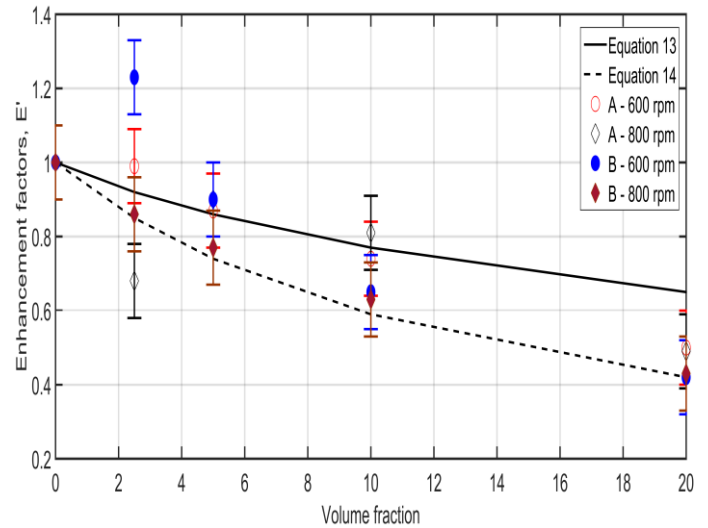


Figure 4: Experimental versus predicted enhancement factors for oxygen absorption into an n-alkane/water emulsion with solubility ratio ($m = 7.9$) – cases A [28] and B [14].

CONCLUSION

The introduction of an immiscible oil phase to an aqueous phase is known to enhance the solubility of poorly water-soluble gases such as oxygen. The overall volumetric mass transfer coefficient, on the other hand, has been reported to either increase, decrease or remain constant with increase in the volume fraction of the oil phase. By accounting for changes to the emulsion's solubility in the formulations employed for the dynamic method, this reported varied behaviour has been replicated on the basis of modified enhancement factor models. A decrease in the overall volumetric mass transfer coefficient has been observed for cases of series mass transfer (with and without shuttling) as well as parallel mass transfer for a system with a diffusivity ratio $0 < D_r < 1$. Constant or enhanced values of the overall volumetric mass transfer coefficient have been observed for cases of parallel mass transfer in systems with diffusivity ratios equal to or greater than 1 respectively. Two case studies have been employed to illustrate the validity of this modelling approach. The modified enhancement factor models have been shown to be accurate to within 10% of experimental results, especially at large oil phase volume fractions ($x > 5\%$). These models can be used as the basis for future empirical and predictive studies on mass transfer by the dynamic method in both gas-liquid-liquid and gas-liquid-liquid-solid systems.

ACKNOWLEDGEMENTS

The support of the DST-NRF Centre of Excellence in Catalysis towards this research is hereby acknowledged. Opinions expressed and conclusions arrived at, are those of the author and are not necessarily to be attributed to the CoE.

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APPENDIX

Cesário, Beverloo et al. [24] performed a theoretical analysis for an assumed steady state semi-batch reactor and obtained the expression;

$$\frac{F}{V}(C_g^{in} - C_g^{out}) = K_L a' (C^* - C) = K_L a'' (C_w^* - C_w), \quad (A1)$$

where

$$K_L a'' = K_L a' \cdot (1 - x + xm) \quad (A2)$$

from the definition of saturation concentration in equation (2).

In the above equations, F is the gas feed rate and V is the volume of the emulsion. C_g is the solute gas' concentration in the gas phase and superscripts *in* and *out* refer to the inlet and outlet of the reactor respectively. Other terms are as previously defined.

Cesário, Beverloo et al. [24] illustrated that another measure of the overall mass transfer coefficient ($K_L a''$) could be obtained. This $K_L a''$ value increased with an increase in volume fraction of the oil phase whereas their $K_L a'$ values did not vary significantly as illustrated in Figure 3. They proposed that previously reported enhancements in the overall mass transfer coefficient [30] could be explained by equation (A2).