Oxygen mass transfer in a high solids loading three-phase internal-loop airlift reactor

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The way volumetric mass transfer coefficient in a 60 L three-phase internal-loop airlift reactor with an enlarged degassing zone is influenced by the airflowrate (riser superficial gas velocities between 0.01 and 0.5 m/s), solids loading (up to 30% v/v), solids density (1023 and 1048 kg/m^3) and the liquid phase properties was studied. The increase of the airflow rate and the introduction of ethanol enhanced the volumetric mass transfer coefficient in the system. The opposite effect was observed with the progressive introduction of solids and a small increase on solids density. Correlations for the volumetric mass transfer coefficient with the riser superficial gas velocity and solids loading were established, for the two solids density and the two liquid-phases.

Introduction

The primary purpose of a bioreactor is to provide such environmental conditions to the microrganism that it will carry out the required reaction or transformation optimally [1]. In aerobic systems, the critical limiting factor in providing the optimal environment is the oxygen mass transfer, as a consequence of the low solubility of oxygen in fermentation media. Hence, the volumetric mass transfer coefficient ($k_L a$), which is normally used to characterize the mass transfer performance, plays an important role in the performance of bioreactors [1-3]. Ideally, a reactor should have a maximum mass transfer rate, at an efficient mixing and at a minimum energy input [2]. Several studies have demonstrated the airlift reactors ability to provide this [1, 2, 4]. However, the data presented in the literature for mass transfer in airlift reactors vary widely and is sometimes contradictory due, probably, to the wide range of reactors studied and differences in experimental techniques used [2, 3]. Most experimental measurements [5, 6] have shown that the rate of mass transfer in an airlift reactor is influenced by various design (*i. e.*, bioreactor type and geometry), system (*i. e.*, fluid properties) and operation (*i. e.*, liquid and gas velocity and gas holdup) variables.

Fluid coalescence properties can vary between two extreme cases: coalescing and non-coalescing. Fermentation liquids will always be between the two extremes. However, due to their complex composition, it is impossible to predict where ";between"; [5]. Once released from the sparger, the bubbles are subjected to the dispersion and the coalescence processes, what will influence their size. Therefore, studies have shown that liquids differing from water on the surface tension, density, viscosity and ionic strength affect gas holdup and the overall mass transfer coefficient [1], being its influence dependent on the reactor type.

The use of gas-liquid-solid three-phase reactors has been widespread in chemical processing

and those containing low-density particles are finding applications in several biotechnology processes [6]. One of the most important features of these processes is that, in general, suspended solids, including microorganisms immobilized on solid-support particles and agregated in flocs and pellets, have a density very close to that of the liquid medium, which may, sometimes, change during the process. However, only a few studies have addressed these aspects in three-phase airlift reactors [6-9]

The presented results describes the way volumetric mass transfer coefficient in a internal-loop airlift reactor with a degassing zone is influenced by changing system and operation variables that have been previously shown to affect hydrodynamic variables directly related with the mass transfer: the liquid-phase, the solids loading, the solids density and the airflow rate [10,11]

Experimental

Experiments were performed in an 60 L internal-loop airlift reactor of the concentric tube type (fig. 1), with an enlarged degassing zone, constructed according to results obtained by Vicente and Teixeira [12] in what concerns the effect of design parameters on solid circulation.

Riser superficial gas velocities studied were between 0.01 and 0.5 m/s. Water and a 10 g/L aqueous solution of ethanol were used as liquid-phase and Ca-alginate beads, with two different densities, were used as solid-phase and prepared according to the procedure described by Vicente and Teixeira [12]. The mean diameter and density of the ";low density solids"; (LD) were 2.131 ± 0.102 mm and 1023 ± 1 kg/m^3, respectively, and the values for the ";high density solids"; (HD) were 2.151 ± 0.125 mm and 1048 ± 1 kg/m^3. Solids loading applied was 0%, 5%, 10%, 15%, 20% and 30% (v/v).

Two polarographic dissolved oxygen electrodes (Mettler Toledo T-type) connected to dissolved oxygen meters (Mettler Toledo O$_2$ 4100) used to measure dissolved oxygen concentration that was recorded using a PC based data acquisition system. The volumetric mass transfer coefficient $k_L a$ was determined by the dynamic method described by Chisti [1] and Benyahia *et al.* [3]. using the first order model [1]:

$$\frac{C^*-C_L}{C^*-C_{LO}} = 1 - E = \left(\frac{e^{-tk_L a}}{t_E} - k_L a e^{-\frac{t}{t_E}} \right) \cdot \frac{t_E}{1-t_E k_L a} \tag{1}$$

where E is defined as:

$$E = \frac{C_L - C_{LO}}{C^*-C_{LO}} \tag{2}$$

and t_E is the electrode time delay. For $t >> t_E$, equation 1 reduces to:

$$1 - E = \frac{e^{-tk_L a}}{1-t_E k_L a} \tag{3}$$

In this work, values of the volumetric mass transfer coefficients ($k_L a$) were calculated as the slope of the $-\ln(1-E)$ vs. t plots and the time delay (t_E) from the y-intercept = $\ln(1-t_E k_L a)$.

According to Van't Riet [13], the electrode response time would have to be much smaller than the mass transfer response time of the system $1/k_La$ to be neglected. In practice, this is seldom the case.

For each experimental condition, three replicates were done and the volumetric mass transfer coefficient was the medium value of the values obtained for the two electrodes in the three replicates.

Results and Discussion

In this work, the presence of the solid phase negatively influences the mass transfer rate (fig. 2), as was reported by other authors [6, 14, 15]. Independently of the liquid-phase and the solids density, k_La diminishes with the increase of solids loading, essentially for riser superficial gas velocities higher than 0.075 m/s. The reduction on the volumetric mass transfer coefficient is probably the result of the coalescence process, increased by the increase of the amount of solids as reported in Freitas and Teixeira [9], what leads to a decrease on the interfacial area a. According to Verlaan and Tramper [7], the effect on the mass transfer coefficient k_L will be of minor importance.

Up to 0.075 m/s, the effect of solids loading on k_La is negligible, once the amount of gas in the reactor is so small that the solids interference in the coalescence process is not significant.

Comparing to the works of Komáromy and Sisak [15] and of Siegel *et al.* [16], where reductions of 25% were obtained with solids loading of 20% and 30%, respectively, the reductions of k_La in the present work are very high. In cases where 30% of solids could be worked with, reduction in k_La ranged from 60 to 70% and, even in the cases where maximum solids loading was 20%, reductions of k_La of 40% to 70% were obtained. It is also shown that by adding ethanol to water (a coalescence inhibitor) the volumetric mass transfer coefficient is significantly enhanced, for riser superficial gas velocities higher than 0.075 m/s. This increase on k_La must be due to an increase in specific interfacial area, since on addition of alcohols the mass transfer coefficient k_L decreases, by yielding an additional resistance to the interfacial mass transfer [17,18]. As alcohols are inhibitors of coalescence, bubble size decreases and the specific interfacial area increases.

According to Onken and Weiland [19] and Weiland [20], the addition of compounds that reduce bubble coalescence increases the volumetric mass transfer coefficient by a factor of about two. In our case, for riser superficial gas velocities up to 0.075 m/s, the augment is very small, while for higher airflow rates, values of k_La for aqueous ethanol solution are 1.5 to 2 times the values obtained with water.

The effect of the airflow rate and solids density on the volumetric mass transfer coefficient (k_La) for water (a) and aqueous ethanol solution (b) was also verified. The k_La value increases with an in increasing riser superficial gas velocity (u_{gr}), which is due to the higher gas holdup, as was reported in Freitas and Teixeira [10, 11]. As for the gas holdup, the increase of k_La is more pronounced for values of superficial gas velocity up to 0.167 m/s. In spite of the higher amount of gas inside the reactor as the airflow rate increases, coalescence occurs more easily for high airflow rates, counterbalancing the increase on gas holdup.

Observing values of mass transfer coefficient for both solids density, it can be seen that a small increase on solids density leads to a significant reduction on k_La (Fig. 2), specially for high riser superficial gas velocities. An enhancement of riser and downcomer solids holdup with increasing

solids density was observed in a previous work [10]. For that reason, coalescence increases due to the diminishing of the flux area for the gas and liquid phases, what is reflected in a smaller interfacial area *a*. If we compare the influence of solids density on the volumetric mass transfer coefficient for water and aqueous ethanol solution, it seems that the decrease on $k_L a$ with solids density is higher for the aqueous ethanol solution. This is in agreement with the results previously obtained by the authors [11], where it was observed that the decrease of riser and downcomer gas holdup with solids density is also more pronounced for the ethanol solution. Consequently, this is reflected in the results of volumetric mass transfer coefficient.

The volumetric mass transfer coefficient was correlated to the riser superficial gas velocity (u_{gr}) and the solids loading (ε_s), for each liquid-phase and type of solids by:

Water/";Low density solids";:

$$k_L a = \left(-0.93\, u_{gr}^2 + 1.33\, u_{gr} - 0.012\right) \times \left(-0.0000016\, \varepsilon_s^2 - 0.00099\, \varepsilon_s + 0.054\right) \tag{4}$$

Water/";High density solids";:

$$k_L a = \left(-0.33\, u_{gr}^2 + 0.43\, u_{gr} - 0.0064\right) \times \left(0.000080\, \varepsilon_s^2 - 0.0056\, \varepsilon_s + 0.17\right) \tag{5}$$

Ethanol/";Low density solids";:

$$k_L a = \left(-0.95\, u_{gr}^2 + 1.34\, u_{gr} - 0.021\right) \times \left(-0.000072\, \varepsilon_s^2 + 0.00079\, \varepsilon_s + 0.075\right) \tag{6}$$

Ethanol/";High density solids";:

$$k_L a = \left(-0.78\, u_{gr}^2 + 1.20\, u_{gr} - 0.021\right) \times \left(-0.000074\, \varepsilon_s^2 - 0.0035\, \varepsilon_s + 0.081\right)$$

$$0 < u_{gr}\,(m/s) < 0.5$$
$$0 < \varepsilon_s\,(\%v/v) < 30 \tag{7}$$

where

$$0 < u_{gr}\,(m/s) < 0.5$$
$$0 < \varepsilon_s\,(\%v/v) < 30$$

The points given by the correlations together with the experimental values are represented in fig. 3. As can be seen, a good agreement ($\pm 10\%$ for water and $\pm 20\%$ for aqueous ethanol) is obtained between calculated and experimental values.

The low $k_L a$ values reported in this work compared to those in the literature can be justified by the use of a downcomer to riser cross-sectional area ratio (A_d/A_r) greater than 1 [17].

Conclusions

For a three-phase external-loop airlift reactor with an enlarged degassing zone, it was shown that the volumetric mass transfer coefficient diminishes with the increase of solids loading, especially for high airflow rates, due to an increase in bubble coalescence. Reductions between 40% and 70% were obtained with the introduction of 20% and 30% of solids. A significant decrease on $k_L a$ resulting from a small increase of solids density (from 1023 to 1048 kg/m^3) was observed, as a consequence of the effect of solids density on solids distribution in the reactor. A progressive increase on the concentration of solids in the lower sections of the reactor, as riser and downcomer, with the increase of solids density is responsible for the enhancement of coalescence and the consequent decrease on the specific interfacial area.

Airflow rate and the presence of ethanol were shown to enhance the volumetric mass transfer coefficient - airflow rate by primarily increasing gas holdup and ethanol by inhibiting coalescence. The increase on $k_L a$ by the presence of ethanol depends on the amount and type of solids and on the airflow rate.

The volumetric mass transfer coefficient was correlated to the riser superficial gas velocity (u_{gr}) and the solids loading (ε_s), for the two types of solids and for the two liquids, water and ethanol solution. Agreements between the calculated values and the experimental data of ±10%, for water, and of ±20%, for aqueous ethanol, were obtained.

Nomenclature

a	Gas-liquid interfacial area per unit liquid volume	(1/m)
A_d	Downcomer cross-sectional area	(m^2)
A_r	Riser cross-sectional area	(m^2)
C^*	Saturation (or equilibrium) dissolved oxygen concentration	(kg/m^3)
C_L	Instantaneous concentration of oxygen in liquid	(kg/m^3)
C_{L0}	Initial concentration of oxygen in the liquid	(kg/m^3)
k_L	Mass transfer coefficient	(m/s)
t	Time	(s)
t_E	Electrode delay	(s)
u_{gr}	Riser superficial gas velocity	(m/s)

Greek symbols

ε_s Solids loading

Most of the data presented in this work will be published in Chemical Engineering Journal
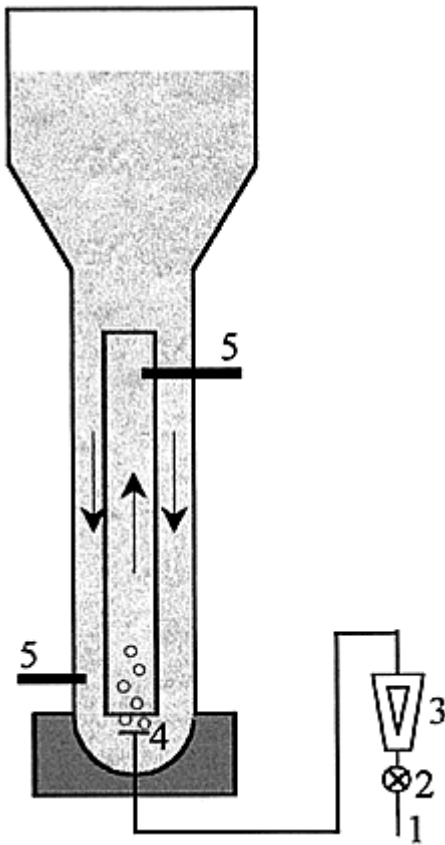
Figure 1: Schematic representation of the experimental airlift reactor (1-air feed; 2-regulation valve; 3- rotameter; 4-sieve plate; 5 - oxygen electrodes)
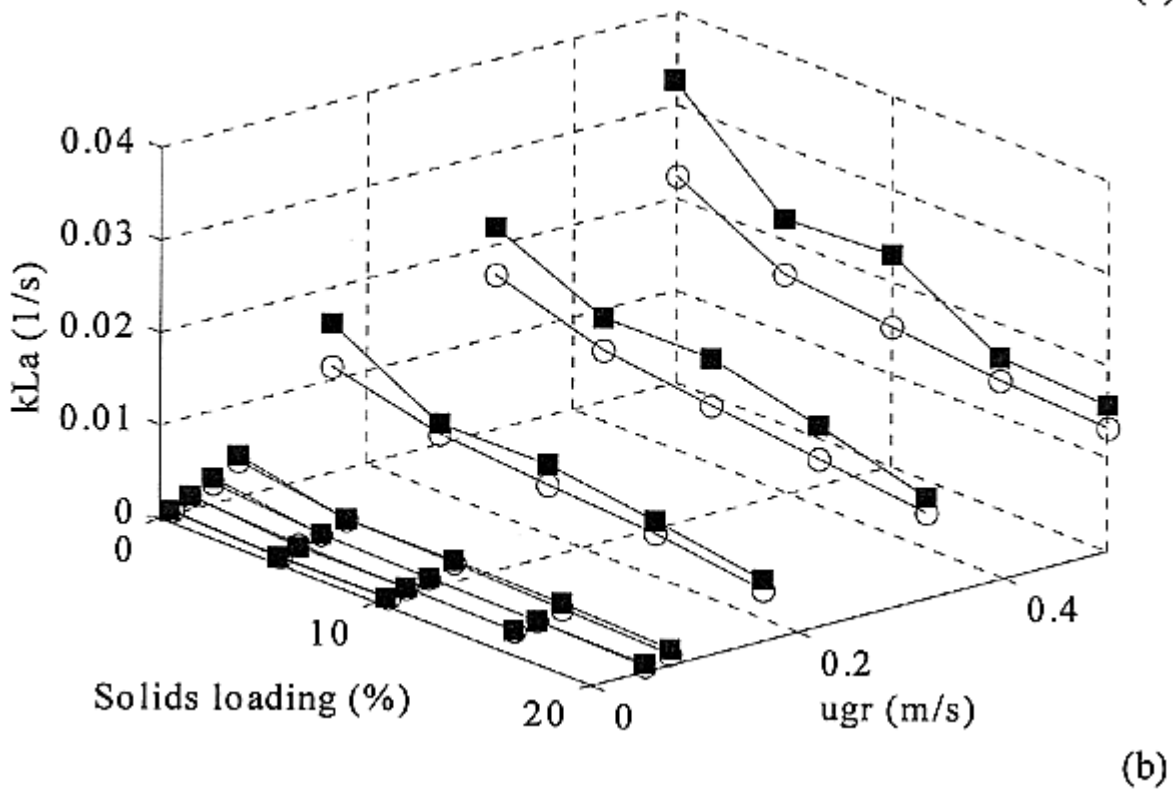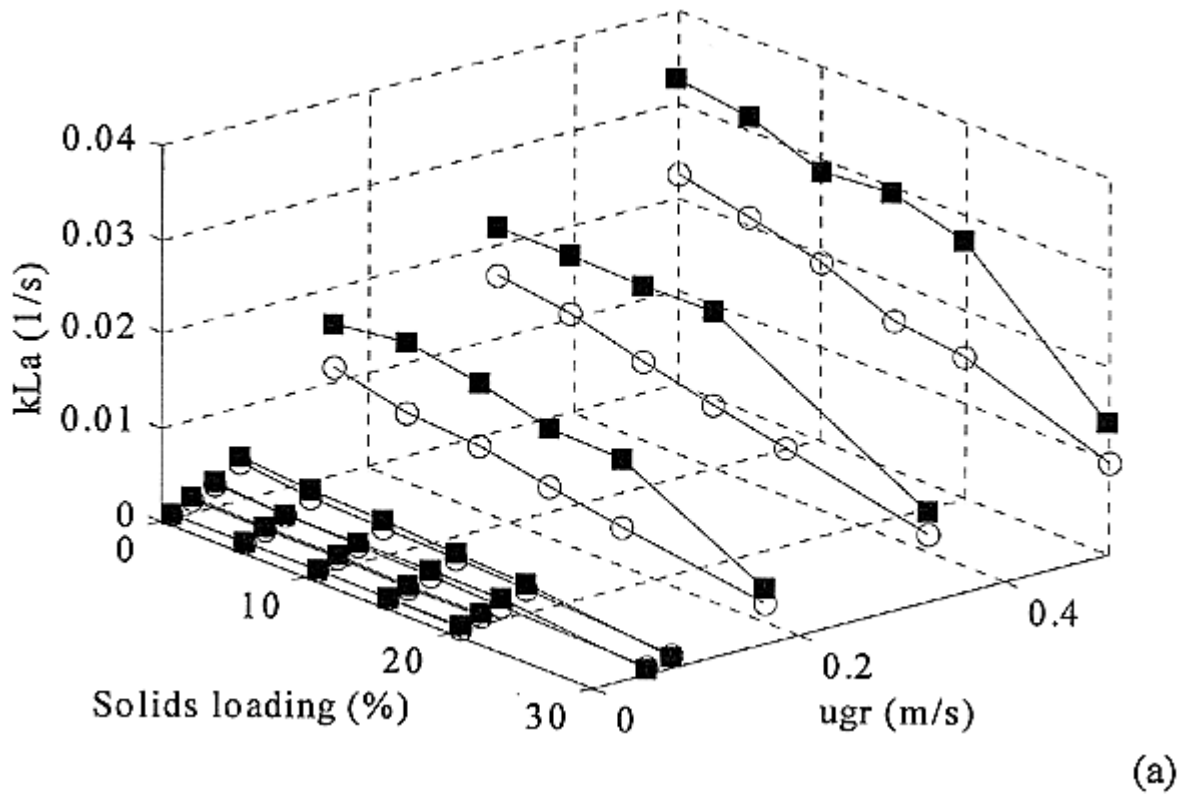
Figure 2: Volumetric mass transfer coefficient ($k_L a$) **vs**. solids loading and riser superficial gas velocity (u_{gr}), for water (O) and the aqueous ethanol solution (n): (a) ";low density solids";; (b) ";high density solids";
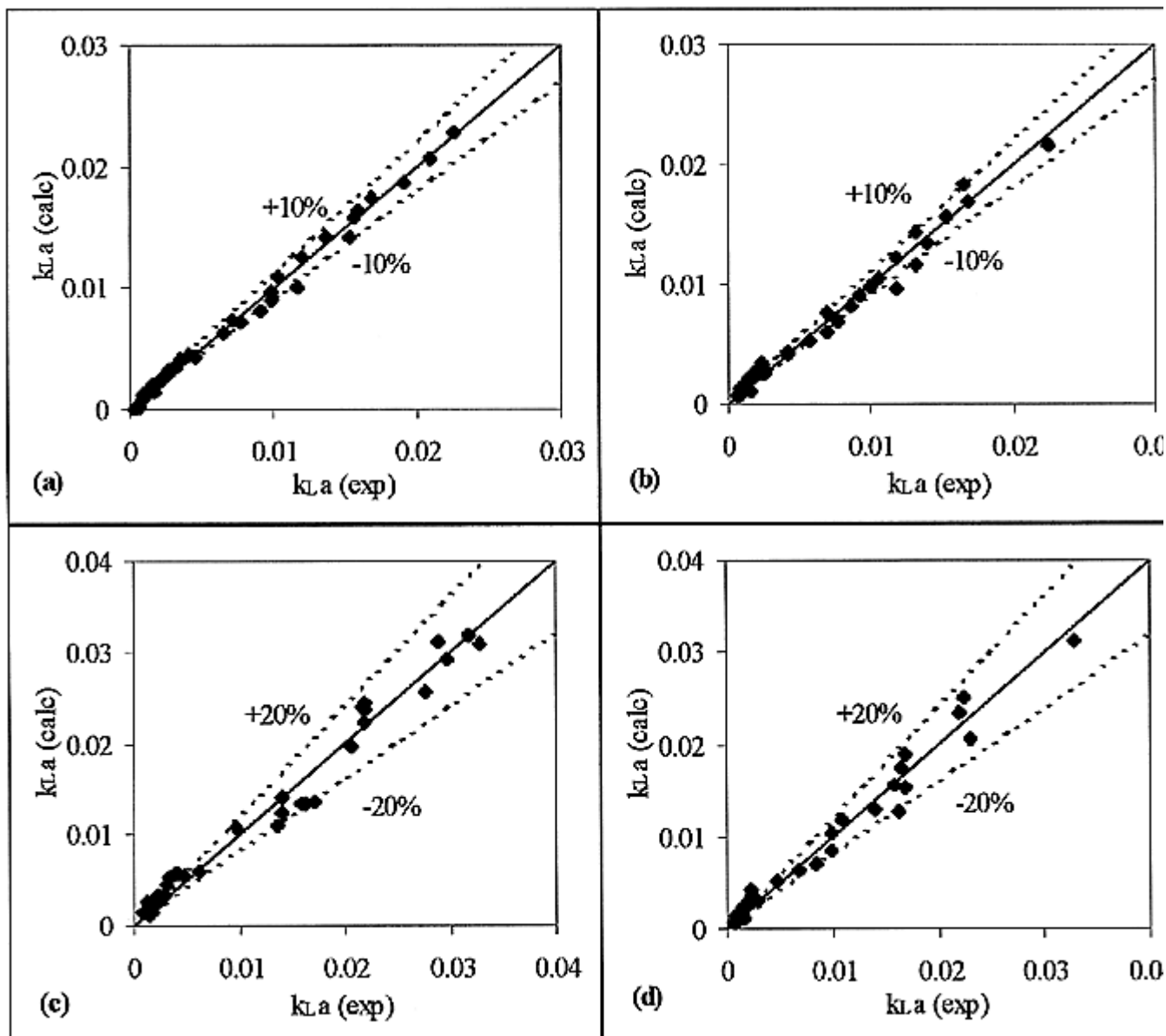
Figure 3: Comparison between calculated $k_L a$ values and experimental data: (a) water/";low density solids";; (b) water/";high density solids";; (c) aqueous ethanol solution/";low density solids";; (d) aqueous ethanol solution/";high density solids";

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