Fast determination of gas-liquid diffusion coefficient by an innovative double approach

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Feishi Xu, Mélanie Jimenez, Nicolas Dietrich *, Gilles Hébrard

LISBP, Université de Toulouse, CNRS, INRA, INSA, Toulouse, France

HIGHLIGHTS

- Innovative double approach for diffusive coefficient measurement.
- Generalization of the PLIFI technique with oxygen field analysis.
- Simple one-probe measurement technique in a Hele-Shaw cell.
- Validation of both methods with visualization characterization.
- Fast determination of gas-liquid diffusion.

ARTICLE INFO

ABSTRACT

Two effective mathematical approaches based on the probability and statistics theory are proposed for obtaining the oxygen diffusion coefficients in gas-liquid systems. The first method was to apply PLIFI (Planar Laser Induced Fluorescence with Inhibition) to the wake of an isolated bubble rising in water. The chi-squared distribution was introduced to describe the concentration field of oxygen diffusion. The approach provided a feasibility to evaluate the gas-liquid diffusion coefficient by analyzing the temporal evolution of the oxygen spot area on the experimental images. The second method was conducted through a flat air-liquid interface in a Hele-Shaw cell filled with quiescent deoxygenated water. By analogy, the evolution of the oxygen concentration with time was demonstrated to be characterized by the law of inverse gamma. The diffusion coefficient was estimated from the dissolved oxygen concentrations measured by a Clark-type probe at a specific position in the liquid phase. This technique was also tested experimentally for different probe locations to minimize their influence on the diffusion coefficient determination. Moreover, the non-perturbation property of the technique was validated by visualizing the oxygen concentration field around the probe through the colorimetric method. The diffusion coefficients of oxygen in water calculated from the two measurements were almost identical: $2.00 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$ which is in good agreement with the literature. The specificity of these two methods is that they do not require the properties of the fluid (such as the saturation concentration) or to calibrate the probe. Thus, it provides an alternative approach to evaluate the gas-liquid coefficient accurately and quickly, even in the complex media cases, such as biological media.

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1. Introduction

The quantification of mass transfer phenomenon is important in the industry. The determination of physical properties in the transport process, such as the diffusion coefficient and liquid-side mass transfer coefficient, would be helpful to understand the transport mechanism deeply. Concentrating on the diffusion regime which is characterized by a diffusion coefficient D, it physically represents a migration of molecules of a constituent under the effect of a potential chemical gradient. The first law of diffusion was established by Fick (1855). By analogy with Fourier's law governing the transfer of heat, the diffusive flux can be expressed as

$$J = -D\nabla C \tag{1}$$

where J is the diffusive flux ($\mathrm{kg\,m^{-2}\,s^{-1}}$) and ∇C denotes the concentration gradient. The subsequent researches in this domain are intensive and several measurement techniques have been developed: the steady state method (Tham et al., 1967), capillary cell method (Gubbins et al., 1966; Malik and Hayduk, 1968), laminar

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Nomenclature

Latin symbols

C	concentration (kg/m^3)
D	diffusion coefficient (m^2/s)
d_{eq}	equivalent bubble diameter (m)
I_0	fluorescence intensity without quencher, gray level
I_Q	fluorescence intensity with quencher, gray level
J	diffusive flux (kg/m^2 s)
k	freedom degrees
K	Stern-Volmer constant (m^3/kg)
M	quantity of mass per unit area (kg/m^2)
$[O_2]$	oxygen concentration (kg/m^3)
P	probability
$[Q]$	quencher concentration (kg/m^3)
R	radius of the image spot (m)
r	radius (m)
Re	reynolds number
S	surface of the spot in the image (m^2)
t	time (s)
x	abscissa (m)
y	ordinate (m)

Greek symbols

Γ	gamma function
λ	threshold factor
δ	length of a pixel on the recorded image (m)
σ	standard deviation
τ	lifetime of the fluorescence molecule with inhibition (s)
τ_0	lifetime of the fluorescence molecule without inhibition (s)

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jet method (Duda and Vrentas, 1968; Ferrell and Himmelblau, 1967), and absorption measurement (Sovová and Procházka, 1976). Other techniques based on the Taylor dispersion (Baldauf and Knapp, 1983), the use of polarographic sensors (Ho et al., 1986; Ju and Ho, 1985) and bubble size calculation (de Blok and Fortuin, 1981; Wise and Houghton, 1966) can also be considered. However, the classical determination methods present some limitations due to hydrodynamic perturbation, natural convection, necessity of transparent liquids, long response time, impact of the liquid media, and so on (Blackadder and Keniry, 1973, 1974). Furthermore, it has to be noted that most of the measurements concern gas-gas or liquid-liquid systems and the knowledge of the case persisting in the gas-liquid system is not sufficient.

More recently in laboratories, the technique by using microprobes has been adopted because of its simplicity of experimental configuration (Bowyer et al., 2004; Jamnongwong et al., 2010). For instance, Hebrard et al. (2009) assessed the impact of surfactants on the oxygen diffusion coefficient with a Clark-type probe in a stirred cell. This kind of technique always requires the insertion of measuring instruments (ex. pressure, concentration meters) which may bring a perturbation to the system. Due to the non-intrusive advantages, optical techniques such as interferometry (Guo et al., 1999), are developed to characterize the diffusive process. The technique of interferometry could quantify the transfer in a liquid phase through the change of refractive index induced by the presence of dissolved gas (Roetzel et al., 1997; Wylock et al., 2011). However, the process for obtaining the relation between the refractive index and dissolved gas concentration is always complicated and time-consuming. The planar laser-induced fluorescence (PLIF) is another optical method widely applied to characterize the mass transfer in the gas-liquid system (Bouche et al., 2013; Sancho et al., 2016; Stamatopoulos et al., 2015). The principle of PLIF is to introduce a fluorescent dye into the liquid phase illuminated by a laser sheet. According to the properties of different fluorescent dyes, the fluorescence intensities can be affected by one or multiple the fluid conditions (the presence of specific gas, pH value, and temperature). The state of mass transfer can thus be obtained from images of the studied solution in the enlightened area recorded by cameras. Due to the advantages (ex. fast response, no flow disturbance, high resolution), several PLIF-based studies have been carried out to evaluate the gas-liquid diffusion coefficient (Bork et al., 2005; Dietrich et al., 2015; Jimenez et al., 2012a,b) with good accuracy.

Overall, techniques to measure the diffusion coefficient are diverse, each of which displays low measurement uncertainties. Nevertheless, if a comparison is made between the diffusion coef-

ficient values obtained by these techniques, a big gap appears. For example, the values in the literature for the diffusion coefficient of oxygen in water range between $0.7 \times 10^{-9} \, m^2 \, s^{-1}$ and $2.5 \times 10^{-9} \, m^2 \, s^{-1}$ for a given temperature (20 °C). The empirical equations or semi-empirical ones, commonly used in the literature and the industry, being established from these experimental results, it is not surprising that their validity is, in some cases, questionable.

Therefore, the objective of this study is to provide new insight into this domain. Two different methods are proposed to obtain the diffusion coefficient of oxygen in water in different devices. In the first method, PLIF with inhibition (PLIFI) technique was used to measure the mass transfer in the wake of an isolated bubble rising in a column. In the second one, a probe was used to measure the concentration of dissolved oxygen passed through a flat air-liquid interface in a Hele-Shaw cell. With the experimental data, both diffusion coefficients were calculated based on the effective mathematical models: the chi-squared distribution and the law of inverse gamma, respectively. The final coefficient could be determined by comparing these two results.

2. Materials and methods

2.1. First method: PLIF with inhibition in a bubble column

PLIF is an optical technique which has already been proved powerful for the mass transfer visualization (Asher, 2009; Jimenez et al., 2013). In PLIF with inhibition (PLIFI), the ability of some molecules called "quenchers" to inhibit the fluorescence dye is considered. Oxygen, which is of prime interest in a series of studies (Dani et al., 2007; Jimenez et al., 2013; Kück et al., 2010, 2012), has been known as an excellent quencher. The quenching effect is usually considered to be a consequence of collisions between molecules where the excess energy of the dye is absorbed by oxygen (Lakowicz, 1999). The suitability of PLIFI is mainly because the technique is not only limited to visualization but also enables an accurate quantification of the transferred mass. The quantification of the mass transfer is straightforward since the fluorescence level is directly related to the oxygen concentration in the liquid phase according to the (Stern and Volmer, 1919) equation:

$$\frac{I_Q}{I_0} = \frac{\tau}{\tau_0} = \frac{1}{1 + K_{sv}[Q]} \tag{2}$$

where K_{sv} is the Stern–Volmer constant ($m^3 \, kg^{-1}$), $[Q]$ the quencher concentration ($kg \, m^{-3}$), τ and τ_0 are the lifetimes of the