ELSEVIER

Chemical Engineering Journal 144 (2008) 379–385

Chemical Engineering Journal

www.elsevier.com/locate/cej

Interfacial area evaluation in a bubble column in the presence of a surface-active substance
Comparison of methods

D. Gómez-Díaz*, J.M. Navaza*, B. Sanjurjo

Department of Chemical Engineering, University of Santiago de Compostela, Spain

Received 6 November 2006; received in revised form 4 February 2008; accepted 6 February 2008

Abstract

The influence of a surface-active substance upon the behaviour observed for the gas–liquid interfacial area in a bubble column has been studied employing two different techniques: chemical and photographic methods.

Important differences between the interfacial area values have been found, and they have been assigned to different phenomena existing in this kind of systems, especially the Marangoni and barrier effect.

The experimental results obtained in this work under different operational conditions imply that the chemical method is greatly influenced by the existence of surface tension gradients, and this phenomenon produces high values for the interfacial area.

Keywords: Interfacial area; Interfacial turbulence; Bubble column

---

1. Introduction

In gas–liquid systems where the liquid phase controls the mass transfer – that is, in the absorption of relatively insoluble gases – contact devices that produce an increase of the gas–liquid contact area are used, such as packed and bubble columns, airlift and bubbling stirred tanks [1]. Bubble contactors are frequently used in the chemical industry as absorbers, fermenters and reactors, where heterogeneous reactions (gas–liquid or gas–solid–liquid) [2,3] are carried out. In such systems, the gas is dispersed into the liquid phase in a bubble shape, which leads to the required increased contact area, and the mass transfer occurs during the ascent of the bubbles through the liquid.

Bubble columns are easy to use, although they are difficult to design given the complexity of the flow characteristics and the lack of knowledge regarding their behaviour with different ranges of design parameters. The characteristic design parameters of these systems include the gas–liquid interfacial area, the individual mass-transfer coefficients, the flow regime and the bubbles size distribution. An important number of investigations regarding bubble columns are concerned with the experimental determination of one of the above parameters [4,5]. The interfacial area is a fundamental parameter in the design of absorption equipments on the industrial scale because the knowledge of this parameter is necessary to calculate individual mass-transfer coefficients. The value of the interfacial area can vary depending on the kind of contact device, the physical and chemical properties of the gas–liquid systems, and the operating conditions. For this reason, precise methods are required for the determination of the interfacial area, and these methods can be classified as physical and chemical ones.

Physical methods are based on the modification of some physical property [6,7] whereas chemical methods are based on the study of a reaction with well-known kinetic where the absorption rate is a function of the interfacial gas–liquid area [8].

The aim of this work is comparing the results obtained by two different methods: the sulphite oxidation method (SOM)

---

* Corresponding authors at: Department of Chemical Engineering, ETSE, St/ Lope Gómez de Marzoa s/n, University of Santiago de Compostela, E-15782, Santiago de Compostela, Spain.

E-mail addresses: eqnava1@usc.es (D. Gómez-Díaz), eqnavaza@usc.es (J.M. Navaza).

1385-8947/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2008.02.002

and the photographic method. The influence of the surfactant presence on the interfacial area was also determined for all of them.

2. Materials and methods

Decyltrimethylammonium bromide (DTABr) has been supplied by Fluka [CAS number 2082-84-0] with a purity of ≥98%. Sodium sulphite [no. CAS 7757-83-7] and cobalt sulphate 7-hydrate [no. CAS 10026-24-1] have been supplied by Panreac, with purities of ≥99%.

Surface tension and viscosity of aqueous solutions of DTABr have been determined using a Kruss K-11 tensiometer and a Schott-Geratte AVS 350 capillary viscometer. The experimental procedure is similar than the employed in a previous paper [9].

The study to determine the interfacial area was carried out using the experimental set-up employed in previous works related to the absorption processes [10]. The gas/liquid contactor used in these studies has been a cylindrical bubble column (internal diameter = 7 cm; height = 100 cm), made in methacrylate with a volume of 2.4 L. The gas sparger has been a glass capillary with only one orifice to produce a small number of bubbles that allows analyse carefully the influence of surfactant on bubbles size.

In the case of the sulphite oxidation method, the absorption process has been carried out at 25 °C. The gas to be absorbed, oxygen, was passed through two “humidifiers” at 25 °C to prepare the gas phase. This procedure removed other resistance to mass transport and allowed only the evaluation of the liquid phase resistance to the gas transfer. Pure water was placed into the “humidifiers”. The gas flow-rate was measured and controlled with mass flow controllers (5850 Brooks Instruments). The mass flow controllers employed in the present study for the gas flow-rate and pressures ranges, were calibrated by the supplier.

The sulphite oxidation method is based on the oxygen flow-rate absorbed by the liquid phase, consisting in an aqueous solution of sodium sulphite that reacts with the previous absorbed gas in the presence of a homogeneous catalyst (cobalt sulphate).

The photographic method applied in this study has been developed using a bubble column with the same gas sparger employed in the chemical method, although using a bubble column with a square geometry (10 cm × 10 cm × 100 cm) to determine the interface area and remove the influence of the cylindrical wall upon this measurement.

The bubble diameter was measured using a photographic method based on images of the bubbles taken along the height of the column, from bottom to top. A Sony (DCR-TRV9E) video camera was used to obtain the images. A minimum number of 80 well-defined bubbles along the bubble column were used to evaluate the size distribution of the bubbles in the liquid phase employed, and for each gas flow-rate that has been used. The Image Tool v3.0 software was used to carry out the necessary measurements of the bubbles geometric characteristics.

3. Fundamentals

3.1. Chemical method (SOM)

Chemical methods used to calculate the interfacial area are based on the study of certain gas/liquid reactions under specific conditions that allow the relation of the absorption rate directly to the interfacial area value. The major drawbacks of the chemical methods are their limitations to certain specific gas/liquid systems and the necessity of knowing certain physicochemical properties. All these properties can be characterized since the absorbed gas reacts with some of the solute in the liquid phase; that is, because absorption is accompanied by chemical reaction of well-known kinetics.

In the present paper the sulphite oxidation method has been chosen to carry out the interfacial area determination because this chemical method has been successfully employed in our research group [11]. According to the sulphite method, the absorption of oxygen in sulphite aqueous solutions has also been widely used as a method to determine the interfacial areas in packed columns, bubble columns and vessels, and biological reactors [12,13]. Oxygen reacts with the sulphite solutions and the sulphite ion is oxidized to sulphate:

$$\mathrm{O_2} + 2\mathrm{SO_3}^{2-} \rightarrow\ 2\mathrm{SO_4}^{2-} \tag{1}$$

and in general, the reaction rate is expressed with the expression shown in Eq. (2).

$$(-r_{\mathrm{O_2}}) = k[\mathrm{O_2}]^m \left[\mathrm{SO_3^{2-}}\right]^n \tag{2}$$

where k is the rate constant.

The conditions (reagents and catalyst concentration) and experimental procedure of SOM method is resumed in a previous work [11] for gas–liquid interfacial area determination.

The procedure to carry out the determination of the absorption rate under the experimental conditions of this work – that will be used for the calculation of the interfacial area between the phases involved in the absorption process – has been determined employing the differences between the inlet and outlet oxygen gas flow-rate. Some experimental values of interfacial area obtained using this methodology have been compared with other ones calculated using the temporal variation of sulphite concentration by titration with iodine [14].

3.2. Photographic method

The images (i.e., Fig. 1) we obtained of the bubbles in the liquid phases employed show an ellipsoid shape.

For this reason, major (E) and minor (e) axes of the projected ellipsoid (in two dimensions) were determined. The diameter of the equivalent sphere (Eq. (3)) was taken as the representative bubble dimension.

$$d = \sqrt[3]{E^2 \cdot e} \tag{3}$$

Different authors recommend to use the Sauter mean diameter (d_{32}) [15], which is possible to determine using the data

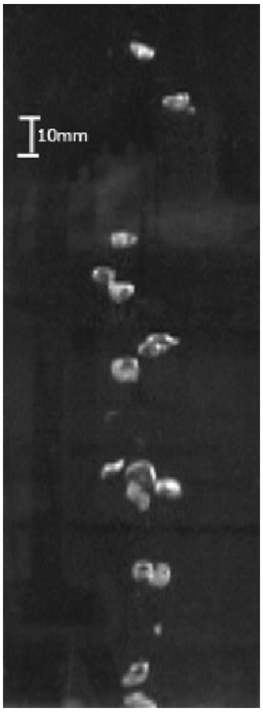

Fig. 1. Image obtained for interfacial area determination using the photographic method. [DTABr] = 10^{-5} mol L^{-1}. $Q_g = 24$ L h^{-1}.

calculated for the equivalent diameter.

$$d_{32} = \frac{\sum_i (n_i d_i^3)}{\sum_i (n_i d_i^2)} \qquad (4)$$

where n_i is the number of bubbles that have an equivalent diameter (d_i).

The Sauter mean diameter and the gas hold-up values allow the calculation of the specific interfacial area using Eq. (5) [16].

$$a = \frac{6\varepsilon}{d_{32}(1-\varepsilon)} \qquad (5)$$

The overall gas hold-up, ε_G, was measured using the volume expansion method:

$$\varepsilon_G = \frac{\Delta V}{\Delta V + V_L} \qquad (6)$$

where V_L is the ungassed liquid volume and ΔV is the volume expansion after gas dispersion, calculated from the liquid level change and the cross-sectional area. The change in the volume in the bubble column was calculated based on the change observed in the liquid level and the increase in this value after gassing.

4. Results and discussion

The first step carried out in the present study has been related with the suitable application of both methods for the interfacial area determination (SOM and photographic). We have carried out experimental measurements to determine the interfacial area generated into the employed bubble column, using different liquid phases. The gas flow-rate fed to the gas–liquid contactor has also been changed. The experimental results obtained are shown in Fig. 2, that allow us to extract two conclusions:

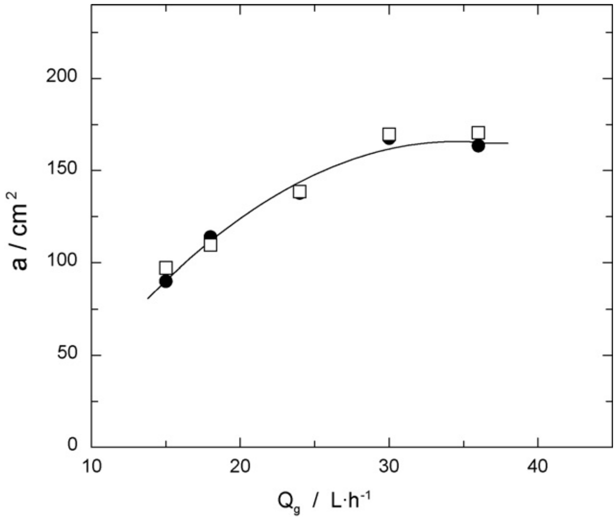

Fig. 2. Interfacial area in the bubble column determined using the photographic (●) and chemical (□) methods.

(i) An increase in the gas flow-rate produces an increment in the interfacial area value until a certain gas flow-rate value from the area is constant. An increase in this operation variable produces, in the low values of gas flow-rate, an increase in the number of bubbles (hold-up) that produces an increment in interfacial area. When high gas flow-rates fed were employed, an increase in the number of bubbles was also observed, but coalescence was detected due to the effective collision of bubbles that generate an increase in bubble diameter, producing then a decrease in interfacial area.

(ii) Differences between experimental values calculated for interfacial area using both methods were not detected, which implies the right use of SOM and photographic methods, and the good results contributed by both methods.

Taken into account the validity of the methods employed in the present work for gas–liquid interfacial area determination, the next step in this research is using DTABr aqueous solutions as liquid phase in the bubble column to determine the influence of the presence of a surfactant upon the value of interfacial area generated into the gas–liquid contactor.

Fig. 3 shows the experimental results obtained for the absorption molar flow in aqueous solutions of sodium sulphite in the presence of cobalt sulphate (as catalyst), when the gas flow-rate was changed using an aqueous solution of DTABr employed as absorbent phase. The experimental results indicate that the mass transfer process is higher when the gas flow-rate increases, as well as the presence of small quantities of DTABr in the liquid phase produces and enhancement of the oxygen mass transfer.

Fig. 3 also shows that the increase in absorption (parameter related to the value of interfacial area in SOM method) produced by the increment of gas flow-rate does not reach a constant value when aqueous solutions of higher DTABr concentration are employed as absorbent phase, because a continuous increase

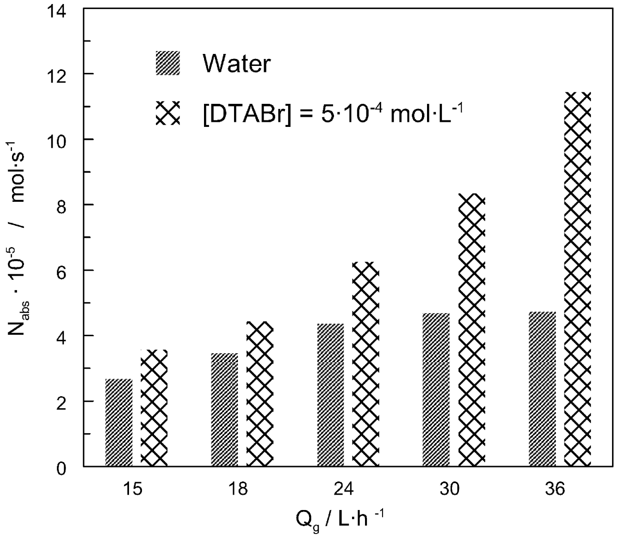

Fig. 3. Influence of gas flow-rate fed to the bubble contactor and DTABr concentration upon the absorption rate employing the chemical method.

was observed. These results indicate that the presence of DTABr could produce some effect that increases the mass transfer rate.

Similar experimental studies have been carried out to analyse the effect of DTABr concentration in the liquid phase upon the interfacial area determined using the chemical method (SOM), and results are shown in Fig. 4. This figure (Fig. 4) shows that an increase in DTABr concentration produces an increase in the interfacial area value – or in the absorption rate – until a maximum (different for each gas flow-rate employed), producing a decrease at high values of DTABr concentration in the studied range. This behaviour has been observed for each value of the gas flow-rate employed.

The behaviour shown in Fig. 4, related to the increase in interfacial area when the surfactant concentration increases (at low concentration range), is in disagreement with previous studies developed to analyse the influence of surface-active substances in absorption processes, using the photographic method to determine de interfacial area [5]. These studies have observed a continuous reduction in the value of interfacial area when the surfactant concentration increases in the liquid phase. However, other studies that employ this method have detected an increase in this value when the surfactant concentration increases [17].

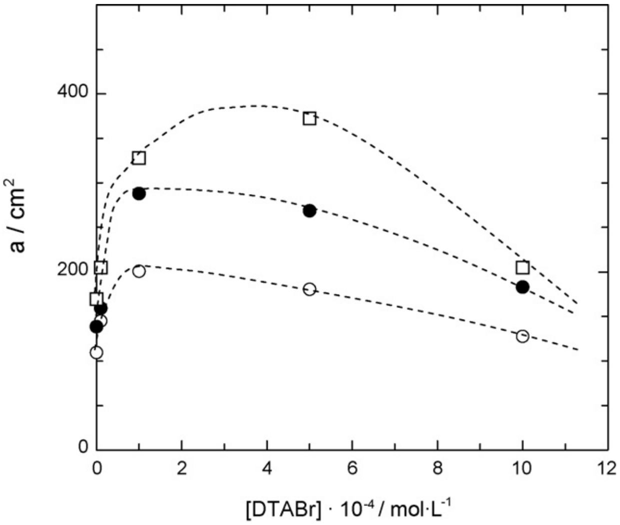

Fig. 4. Influence of surfactant concentration and gas flow-rate upon the interfacial area value. (○) $Q_g = 18\,\mathrm{L\,h^{-1}}$; (●) $Q_g = 24\,\mathrm{L\,h^{-1}}$; (□) $Q_g = 30\,\mathrm{L\,h^{-1}}$.

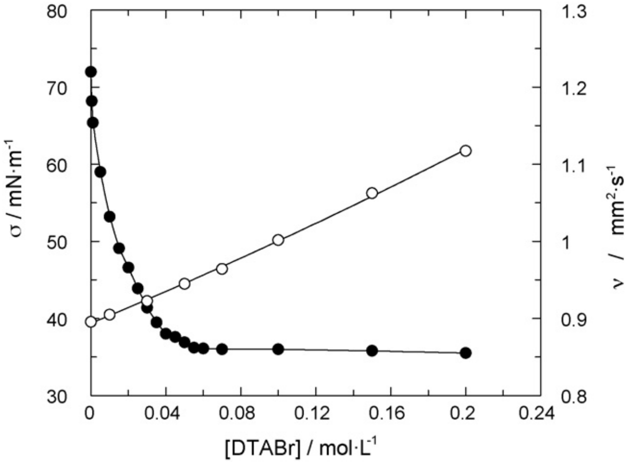

Fig. 5. Effect of surfactant concentration upon the surface tension and viscosity values. (●) Surface tension; (○) kinematic viscosity.

An increase in the interfacial area value, and in the absorption rate corresponding to the oxygen of the liquid phase when the DTABr concentration in the liquid phase increases, is assigned to surface tension gradients due to the decrease in this physical property value by the presence of surfactant molecules at gas–liquid interface (see Fig. 5). The surface tension gradient produces an interfacial turbulence called Marangoni effect [18], which produces an increase in the mass transfer rate, the way our research group has concluded [19,20].

On the other hand, a reduction in the interfacial area value when the maximum is reached was observed, and this decrease in the area, at high values of DTABr concentration in the liquid phase, is due to two different but related effects: the barrier effect that produces a decrease in the mass transfer gas–liquid area, and the reduction on turbulence on liquid film by the presence of surfactant molecules at gas–liquid interface [19]. This is due to the presence of surfactant molecules at the interface, since this solute has a hydrophobic character in the hydrocarbonate chain.

Fig. 4 shows the same behaviour than the previous one observed in Fig. 3, in relation to the effect of the gas flow-rate upon the value of the interfacial area. An increase in the gas flow-rate produces a continuous increase in the gas–liquid interfacial area, although at high values of surfactant concentration the difference between interfacial area for different flow-rates decreases.

The use of photographs of bubbles taken along the bubble column height for interfacial area determination has been carried out. Fig. 6 shows an example of the experimental results obtained for the sphere equivalent diameter distribution.

The bubble size distribution determined for all the experimental conditions has been employed to determine the gas–liquid interfacial area. The effect of the gas flow-rate upon the inter-

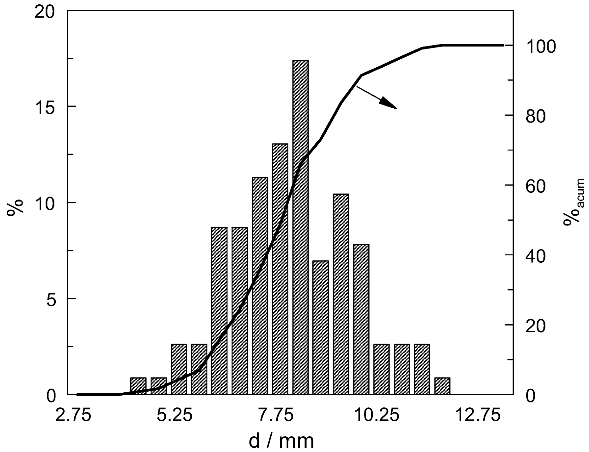

Fig. 6. Bubble diameter distribution in the bubble column. $Q_g = 18\,\mathrm{L\,h^{-1}}$.

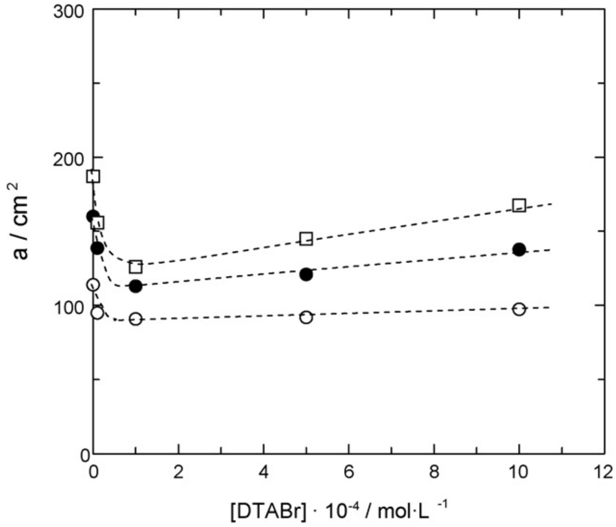

Fig. 8. Influence of surfactant concentration in the liquid phase upon the interfacial area. (○) $Q_g = 18\,\mathrm{L\,h^{-1}}$; (●) $Q_g = 24\,\mathrm{L\,h^{-1}}$; (□) $Q_g = 30\,\mathrm{L\,h^{-1}}$.

facial area determined using the photographic method is shown in Fig. 7, and the experimental results indicate that an increase in the gas flow-rate also produces an increase in the interfacial area. These results are in agreement with the previous ones determined using the chemical method. Data included in Fig. 7 also indicate that the commented effect of the gas flow-rate is the same for all the aqueous solutions employed in this work.

Related to the effect of DTABr concentration upon the value of interfacial area, Fig. 8 shows the results obtained for all the experimental conditions employed in the present work. This figure indicates that a DTABr low concentration liquid phase produces a decrease in the value of the gas–liquid interfacial area, whereas if the DTABr concentration is increased continuously, a slight increase in the interfacial area is observed. The slight increase observed at high DTABr concentration of aqueous solutions is clearer when the gas flow-rate is higher, but it could be consider constant [5].

The decrease in the value of interfacial area at low values of DTABr concentration is assigned to the increase in the bubbles diameter due to the coalescence process, with higher importance in the top section of the bubble column. Different studies have concluded that the reduction in surface tension by the presence of surfactant molecules (Fig. 5) makes the bubble coalescence easy [21].

The obtained experimental values of gas–liquid interfacial area using both methods (chemical and photographic) have been compared, and the obtained results of area for the minor and higher values of gas flow-rate are shown in Figs. 9 and 10. Important differences between the results obtained for both methods have been observed, whereas the experimental results shown in Fig. 2 for till water are similar between them.

The differences observed between the interfacial area results calculated by means of both methods are due to several effects that have an influence upon the mass transfer process. More specifically, the experimental results could be explained on the basis of the Marangoni effect (enhancement of liquid film turbulence), barrier effect and reduction in liquid renewal.

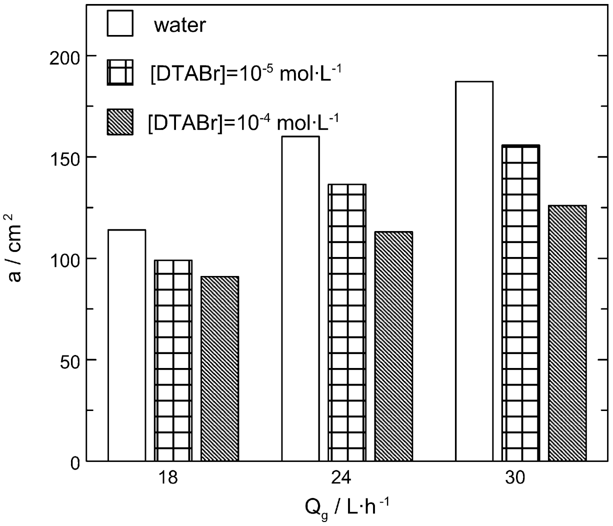

Fig. 7. Influence of gas flow-rate fed to the bubble column and DTABr concentration upon gas–liquid interfacial area (photographic method).

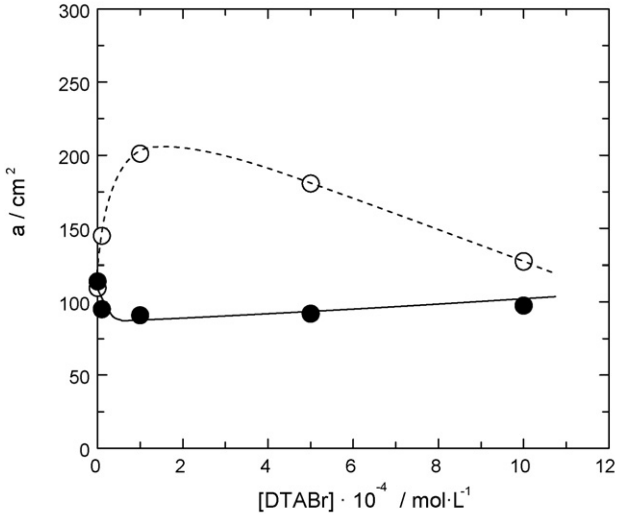

Fig. 9. Comparison between the values of interfacial area determined for both methods. (○) Chemical method; (●) photographic method. $Q_g = 18\,\mathrm{L\,h^{-1}}$.

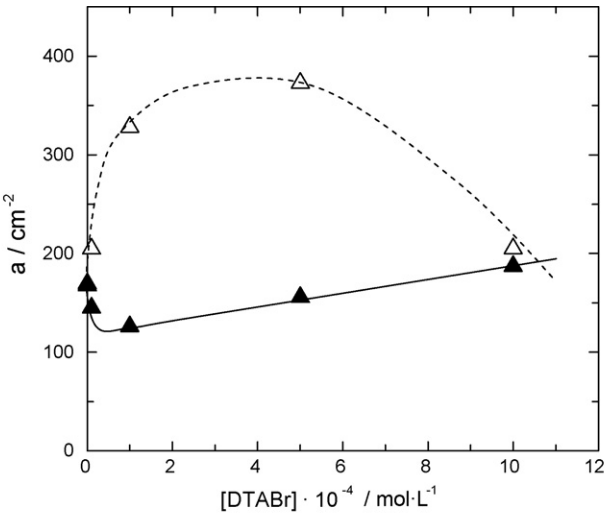

Fig. 10. Comparison between the values of interfacial area determined for both methods. (○) Chemical method; (●) photographic method. $Q_g = 30\,\mathrm{L\,h^{-1}}$.

In the case of the Marangoni effect, it consists in the interfacial turbulence generation near the gas–liquid interface that produces an increase in the mass transfer process. This effect has no real influence upon the interfacial area and it only affects upon the mass transfer coefficient, producing its increase.

On the other hand, the barrier effect consists in a reduction in the interfacial area by accumulation of surfactant molecules in the gas–liquid interface. In this case, this effect must be taken into account in the evaluation of interfacial area since, under certain conditions, it could occupy an important part of the mass transfer area. On the other hand, the presence of surfactant molecules at gas–liquid interface reduces the liquid renewal at gas–liquid interface and this process reduces the mass transfer and then, affects on chemical method results.

The photographic method does not take into account either of the previously commented effects in the determination of the interfacial area, because this hydrodynamic parameter is only determined on the basis of geometrical characteristics.

The experimental values contributed by the chemical method are affected by previously commented effects which act simultaneously but in opposite directions. The Marangoni effect produces an enhancement of the mass transfer rate. Due to the chemical method, that is based on certain experimental conditions that do not include the interfacial turbulence, it allows the calculation of high values for interfacial area in relation to the real value. This behaviour is observed in the experimental results for area obtained using this methodology (see Figs. 4, 9 and 10). We can observe an increase in the interfacial area value when the surfactant concentration increases, because a higher surfactant concentration produces a more important decrease in surface tension (see Fig. 5) which generates the interfacial turbulence.

We can also observe in Figs. 4, 9 and 10 that the effect of surfactant concentration at high values of this variable produces a decrease in the interfacial area value. This clear decrease is due to the higher influence of the negative effects upon the mass transfer process that is sufficient to compensate the interfacial turbulence.

Different calculations of gas–liquid interfacial area occupied by surfactant molecules employing Gibbs isotherm allow conclude that the occupied area by DTABr on gas–liquid interface under the experimental conditions employed in present work is negligible and then, the negative effect caused by the presence of DTABr in the liquid phase is due to the reduction caused on liquid renewal at gas–liquid interface.

The results obtained in the present work for the interfacial area by means of these two methods allow to conclude that they do not contribute real values for the interfacial area, since there must be lower values than the previously ones shown by the photographic method. Due to the low surfactant concentration existing in the liquid phase, it is probable that the values of interfacial area could be similar to the ones calculated using the bubbles' geometrical characteristics (photographic method). Using the chemical method, the effects due to the presence of surfactants in solution introduce great influences upon the interfacial area determination.

References

[1] S.Y. Lee, Y.P. Tsui, Succeed at gas/liquid contacting, Chem. Eng. Prog. 95 (1999) 23–49.

[2] H. Dhaouadi, S. Poncin, J.M. Hornut, G. Wild, Solid effects on hydrodynamics and heat transfer in an external loop airlift reactor, Chem. Eng. Sci. 61 (2006) 1296–1307.

[3] M.V. Dagaonkar, H.J. Heeres, A.A.C.M. Beenackers, V.G. Pangarkar, The application of fine TiO_2 particles for enhanced gas absorption, Chem. Eng. J. 92 (2003) 151–159.

[4] M. Tan, M. Ishii, A method for measurement of local specific interfacial area, Int. J. Multiphase Flow 16 (1990) 353–361.

[5] J.M.T. Vasconcelos, J.M.L. Rodrigues, S.C.P. Orvalho, S.S. Alves, R.L. Mendes, A. Reis, Effect of contaminants on mass transfer coefficients in bubble column and airlift contactors, Chem. Eng. Sci. 58 (2003) 1431–1440.

[6] P. Painmanakul, K. Loubière, G. Hébrard, M. Mietton-Peuchot, M. Roustan, Effect of surfactants on liquid-side mass transfer coefficients, Chem. Eng. Sci. 60 (2005) 6480–6491.

[7] J.S. Chang, E.C. Morala, Determination of two-phase interfacial areas by an ultrasonic technique, Nucl. Eng. Des. 122 (1990) 143–154.

[8] V. Linek, T. Moucha, M. Kordač, Mechanism of mass transfer from bubbles in dispersions Part I. Danckwerts' plot method with sulphite solutions in the presence of viscosity and surface tension changing agents, Chem. Eng. Process. 44 (2005) 353–361.

[9] D. Gómez-Díaz, J.C. Mejuto, J.M. Navaza, A. Rodríguez-Álvarez, Effect of composition and temperature upon density, viscosity, surface tension, and refractive index of 2,2,4-trimethylpentane + cyclohexane + decane ternary liquid systems, J. Chem. Eng. Data 48 (2003) 231–235.

[10] D. Gómez-Díaz, J.M. Navaza, B. Sanjurjo, L. Vázquez-Orgeira, Carbon dioxide absorption in glucosamine aqueous solutions, Chem. Eng. J. 122 (2006) 81–86.

[11] G. Vázquez, M.A. Cancela, C. Riverol, E. Álvarez, J.M. Navaza, Determination of interfacial areas in a bubble column by different chemical methods, Ind. Eng. Chem. Res. 39 (2000) 2541–2547.

[12] G. Vázquez, M.A. Cancela, C. Riverol, E. Álvarez, J.M. Navaza, Application of the Danckwerts method in a bubble column Effects of surfactants on mass transfer coefficient and interfacial area, Chem. Eng. J. 78 (2000) 13–19.

[13] K. Sridharan, M.M. Sharma, New systems and methods for measurement of effective interfacial area and mass transfer coefficients in gas–liquid contactors, Chem. Eng. Sci. 31 (1976) 767–774.

[14] F.K. Kies, B. Benadda, M. Otterbein, Experimental study on mass transfer of a co-current gas–liquid contactor performing under high gas velocities, Chem. Eng. Process. 43 (2004) 1389–1395.

[15] Y.T. Shah, B.G. Kelkar, S.P. Godbole, W.-D. Deckwer, Design parameters estimation for bubble column reactors, AIChE J. 28 (1982) 353–379.

[16] K.V. van't Riet, J. Tramper, Basic Bioreactor Design, Marcel Dekker, 1991.

[17] R. Sardeing, P. Painmanakul, G. Hébrard, Effect of surfactants on liquid-side mass transfer coefficients in gas–liquid systems: a first step to modelling, Chem. Eng. Sci. 61 (2006) 6249–6260.

[18] J.T. Davies, Turbulence phenomena at free surface, AIChE J. 18 (1972) 169–173.

[19] G. Vázquez, G. Antorrena, J.M. Navaza, Influence of surfactant concentration and chain length on the absorption of CO_2 by aqueous surfactant solutions in the presence and absence of induced Marangoni effect, Ind. Eng. Chem. Res. 39 (2000) 1088–1094.

[20] G. Vázquez, G. Antorrena, J.M. Navaza, V. Santos, Absorption of CO_2 by water and surfactant solutions in the presence of induced Marangoni effect, Chem. Eng. Sci. 51 (1996) 3317–3324.

[21] A.H.G. Cents, D.J.W. Jansen, D.W.F. Brilman, G.F. Versteeg, Influence of small amounts of additives on gas hold-up, bubble size, and interfacial area, Ind. Eng. Chem. Res. 54 (2005) 4863–4870.