Gas absorption enhancement by a surface active substance

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The influence of a surface active substance upon absorption process of carbon dioxide in water has been studied in present work. Different low concentration of DTABr have been employed in the liquid phase to study the mechanism of mass transfer observed in a bubble column reactor and the effect upon the absorption kinetics. Different gas flow-rates has been also employed.

1. Introduction
Bubble columns are frequently used as gas-liquid reactors for the manufacture of important products in the process industries (petrochemical, biochemical and chemical engineering). Bubble columns have gained increasing importance in biotechnology, particularly in fermentation and waste water treatment, because bubble columns provide favourable mixing and mass transfer properties combined with low shear stressing of the biological material. In these processes, the mass transfer rates in bubble columns from the gaseous to the liquid phase are sufficiently high. The optimal design of bubble columns of specified geometry requires the analysis and prediction of the effect of various operating variables, i.e. power input, gas flowrate and liquid phase physicochemical properties, on several mass transfer parameters, namely: the overall volumetric mass becomes shorter with increasing liquid surface tension or with increasing liquid viscosity, so the effect of the physical properties of the liquid such as viscosity and surface tension are very important in absorption experiments. The determination of fundamental hydrodynamic parameters, i.e. individual mass transfer coefficients and interfacial area, and their relation with the operating variables, are indispensable to the determination of the mass transfer between the phases, which is necessary for the design and scale-up some kind of devices. Thus, most studies are devoted to the experimental determination of some of these parameters, and more specifically, of volumetric mass transfer coefficient.

The objective of this work is to examine gas-liquid mass transfer in a bubble column in relation with the effect of the effect produced upon the gas / liquid mass transfer by the presence of a surfactant. The influence of liquid properties and superficial gas velocity on volumetric mass transfer coefficient has been investigated.

2. Experimental Section
Decyltrimethylammonium bromide (DTABr) has been supplied by Fluka [CAS number 2082-84-0] with a purity of ≥ 98 %.
2.1. Physical characterization

Density of surfactant aqueous solutions was measured with an Anton Paar DSA 5000 vibrating tube densimeter. This apparatus allows the control of temperature. The kinematic viscosity (ν) was determined from the transit time of the liquid meniscus through a capillary viscosimeter supplied by Schott (Cap Nº 0c, 0.46±0.01 mm of internal diameter, K=0.003201 mm²/s³). An electronic stopwatch with an accuracy of ±0.01 s was used for measuring efflux times. The capillary viscometer was immersed in a bath controlled to ±0.1 °C. The viscometer was a Schott-Geräte AVS 350 Ubbelohde. The surface tension was determined by employing a Krüss K-11 tensiometer using the Wilhelmy plate method. The plate employed was a commercial platinum plate supplied by Krüss. The platinum plate was cleaned and flame dried before each measurement. The surface tension of pure water was determined and compared with the literature to confirm that this method provides suitable results (Alvarez et al, 1998)

The studies of carbon dioxide mass transfer to liquid phases were carried out using a experimental set-up employed by our research group in previous works (Gómez-Díaz et al, 2006) related to the absorption processes. 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 litres. The absorption processes has been carried out at 25 °C. The gas to be absorbed, carbon dioxide, 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. Water was placed into the “humidifiers”. The gas flow-rate was measured and controlled with two mass flow controllers (5850 Brooks Instruments). The mass flow controllers employed in the present study for the gas flow-rate and pressures were calibrated by the supplier. The pressure drop was measured between the column’s inlet and outlet, using a Testo 512 digital manometer. The operational regime was continuous in relation to the gas phase and batch as regards the absorbent liquid.

2.2. Interfacial area determination. Photographic method.

The overall gas hold-up was measured using the volume expansion method, equation 1,

\[ e = \frac{\Delta V}{\Delta V + V_L} \]  

(1)

where \( V_L \) is the un-gassed liquid volume and \( \Delta V \) is the volume expansion after gas dispersion, calculated from the liquid level change and the cross sectional area. In bubble columns, the gas hold-up is simply given by equation 2,

\[ e = \frac{\Delta H}{\Delta H + H_L} \]  

(2)

where \( H_L \) is the un-gassed liquid height and \( \Delta H \) is the increase in liquid level after gassing.
The bubble diameter was measured using a photographic method based on take images of the bubbles along the column height 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 bubbles in the liquid phase employed and for each gas flow rate used.

The Image Tool v2.0 software was used to carry out the necessaries measurements of the geometric characteristics of the bubbles. The images taken for the bubbles in the liquids employed shown a ellipsoid shape. For this reason, major \((E)\) and minor \((e)\) axis of the projected ellipsoid (in two dimensions) were determined. The diameter of the equivalent sphere (equation 3) was taken as the representative bubble dimension.

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

Different authors recommend use the Sauber mean diameter \((d_{32})\) that is possible determine using the data calculated for the equivalent diameter.

\[
d_{32} = \frac{\sum n_i \cdot d_i^3}{\sum n_i \cdot d_i^2} \tag{4}
\]

where \(n_i\) is the number of bubbles having an equivalent diameter \((d_i)\).

The Sauter mean diameter and the gas hold-up values allow calculate the specific interfacial area using the equation 8.

\[
a = \frac{6 \cdot \varepsilon}{d_{32} \cdot (1 - \varepsilon)} \tag{5}
\]

### 3. Results and Discussion

Physical properties determination of liquid phases used in absorption processes is very important to analyse the influence of these physical properties and the presence of different solutes upon the resistance to the gas transport to the liquid phases. For these reasons is necessary attend to the special characteristics of aqueous solutions of surfactants. Figure 1 shows the obtained behaviour upon the influence of surfactant concentration upon the density, viscosity and surface tension. The presence of DTABr produces an increase in the density and viscosity but also produces a decrease in the value of surface tension. The behaviour observed for the last influence is related with the aggregation processes observed in this kind of aqueous solutions. This behaviour has been widely studied suggested the formation of micelles in the zone of surface tension constant value.
In relation with the mass transfer studies developed in the present work, the influence of surfactant concentration and gas flow-rate fed to the contactor. Figure 2 shows and example of the experimental results obtained for the inlet, outlet and absorbed gas flow-rate. The last one has been calculated by difference of the previous ones. The absorbed flow-rate decreases with the operation time due to the liquid phase saturation in carbon dioxide.

Using the experimental data obtained for carbon dioxide absorption rate is possible calculate the carbon dioxide concentration in the liquid phase and its temporal evolution.

In this kind of absorption processes, working in a semi-continuously regime, equation 6 is used to determine the volumetric mass transfer coefficient obtained, using a gas phase mass balance.
\[
\frac{dC}{dt} = k_i \cdot \alpha \cdot (C^* - C)
\]

(6)

where \(k_i\alpha\) is the volumetric mass transfer coefficient, and \(C^*\) and \(C\) are the solubility and carbon dioxide concentration, respectively. In present work, the liquid phases employed such as absorbent phase allow the use of the carbon dioxide solubility data corresponding to gas-water system, in equation 6.

Using the experimental data of gas concentration on the liquid phase, determined by the previously commented methodology, the volumetric mass transfer coefficients \((k_i\alpha)\) have been calculated by means of linear regressions.

![Figure 2. Temporal evolution of molar flow-rates. (○) Inlet; (●) Outlet; (□) Absorbed. \(Q_e = 18 \text{ L}\cdot\text{h}^{-1}\).](chart)

The calculated values for the volumetric mass transfer coefficient under the experimental conditions employed in this work don’t allow obtain all the information about the mass transfer process in a bubble contactor. In this kind of systems, the modifications in the liquid phase could affect simultaneously upon the parameters involved in the volumetric mass transfer coefficient (specific area and mass transfer coefficient).

Different studies about the influence of surfactants upon the gas-liquid interfacial area have concluded that the photographic determination of interfacial area is the better methodology. For this reason our research team has employed this method in the bubble column.

The interfacial area determined previously under different operational conditions has been employed to calculate the mass transfer coefficient and then is possible analyse the effect of surfactants and it concentration upon the mass transfer. Figure M shows the influence of surfactant concentration and gas flow-rate upon the value of mass transfer.
coefficient. The first conclusion obtained using mass transfer coefficient data is the negligible effect of gas flow-rate upon the mass transfer coefficient.

In relation with the influence of surfactant concentration upon the mass transfer coefficient a dual behaviour has been observed: at low surfactant concentration an enhancement in mass transfer has been observed until reach a maximum value. This enhancement is assigned to an increase in interface turbulence due to surface tension gradients. Similar behaviour has been observed by Kim et al (Kim et al, 2006) for other contaminated systems in bubble contactors.

Surfactant concentrations higher than the corresponding to the maximum produce a decrease in the mass transfer coefficient that is due to the reduction in interfacial turbulence by the presence of high surfactant molecules concentration in the gas-liquid interface that reduce the surface renovation.

![Graph showing influence of surfactant concentration upon mass transfer coefficient.](image)

*Figure 3. Influence of surfactant concentration upon mass transfer coefficient. (□) \(Q_g = 18 \text{ L·h}^{-1}\); (●) \(Q_g = 24 \text{ L·h}^{-1}\); (○) \(Q_g = 30 \text{ L·h}^{-1}\).*

**References**

