

## VARIATION OF THE INTERFACIAL AREA DURING CO<sub>2</sub> ABSORPTION INTO ALKANOLAMINES AQUEOUS SOLUTIONS IN A BUBBLE COLUMN REACTOR

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### INTRODUCTION

Bubble columns are widely used in industrial gas-liquid operations (e.g. gas-liquid reactions, fermentations) in chemical and biochemical processes industries, due to their simple construction, low operating cost and high-energy efficiency. In all these processes, gas hold-up and bubble size are important design parameters since they define the gas-liquid interfacial area available for mass transfer. In turn, bubble size distribution and gas hold-up in gas-liquid dispersions depend largely on column geometry, type of gas sparger, operating conditions and physico-chemical properties of the two phases [1]. On the other hand, if the absorption process is accompanied by a fast chemical reaction, the effect of time on the interfacial area should too be analysed.

Dispersion of the gas into the column is a critical in determining the performance of gas-liquid systems. Small bubbles and a uniform distribution over the cross section of the equipment are desirable to maximize the interfacial area and improve transport phenomena [2].

The formation of bubbles at orifices submerged in a liquid has been the subject of many theoretical and experimental works [3,4,5]. In the publications cited above, the main focus of research was on the bubble formation at a single orifice. However, other authors [6] have studied, experimentally, the influence of the distance on the bubble diameter, measuring bubbles at 25 and 45 cm from the sparger in a column 70 cm high.

Despite considerable study of bubble column performance many basic questions concerning the effect of important operational parameters remain unanswered. For instance, although bubble column characteristics have been studied extensively over the last few decades, there is still a fair amount of uncertainty regarding the prevailing mechanisms of bubble formation. Break-up and coalescence of fluid objects play a crucial roles in a broad spectrum of multiphase flow processes such as the evolution of the bubble size distribution in stirred tanks and bubble columns [7]. Consequently, bubble size distribution in a vessel is not constant, but rather, may change due to bubble-bubble interactions leading to breakage or coalescence.

In this work we have studied the absorption process of carbon dioxide into aqueous solutions of different alkanolamines, and we have measured the interfacial area and the gas

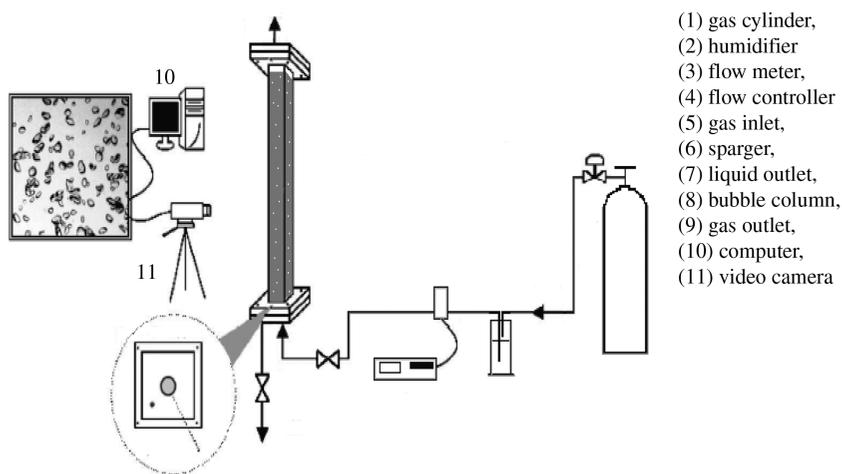
hold-up for all gas-liquid systems studied. In order to check the effect of the reaction time on the interfacial area, four gas flow rates and different concentrations of alkanolamine were used.

### EXPERIMENTAL PROCEDURE

The experimental set-up (Figure 1) consists of a vertical rectangular methacrylate column 1.03 m height (8), having a square cross-section (side length 6 cm). A rectangular geometry was preferred over a cylindrical one because it simultaneously facilitates direct flow visualization and the use of optical measuring methods by minimizing optical distortion. For the injection and uniform distribution of the gas phase (6), a gas sparger, i.e., a porous plate of 4 mm in diameter is installed at the centre of the bottom plate. This plate has another orifice for liquid outlet (7). The gas outlet is situated at the centre of the top plate (9).

Aqueous diethanolamine solutions of different concentrations were employed as liquid phase, while the gas phase was carbon dioxide with a different gas flow rate for each run. The following DEA concentrations were employed: 0.05, 0.1, 0.3 and 1.0 M. Gas flow rates of 10, 15, 20 and 25 L/h were used.

All the experiments were conducted at ambient pressure and temperature conditions. Each experiment run was started by filling the column with appropriate liquid phase up to 100 cm above the sparger. The feed carbon dioxide (1) was passed through a humidifier (2) at the ambient temperature to prepare the gas phase. This procedure removes other resistance to mass transport, thus allowing evaluation of resistance to transfer of liquid phase to gas. The gas flow, before entering the bubble column (5), was



**Figure 1.** Diagram of the experimental set-up

metered by a flow meter (3) and controlled with a flow controller Brooks 0154 (4). All the experiments were performed with no liquid throughput, while the gas phase was injected and distributed into the liquid phase by being passed through the porous plate (6). The gas flow in the outlet was measured with a soap meter.

A high-speed digital video camera (SONY DCR-TRV9E) (11) was used, both, for direct flow visualization, and for bubble size and hold-up measurements. The images obtained were converted into an AVI format file using STUDIO Version 7 software (10). Changes in bubble size over the height of the column were determined by recording images at distances of 20, 45 and 85 cm and above the sparger. The bubble size data was obtained by analyzing the images with the *UTHSCSA Image Tool* software.

## RESULTS AND DISCUSSION

The purpose of this work is to study the variation of interfacial area in a bubble column with the time, the height of the column, gas flow rate and amine concentration. The gas holdup and mean Sauter diameter were extracted by analyzing the images obtained, thus enabling a calculation of the interfacial area.

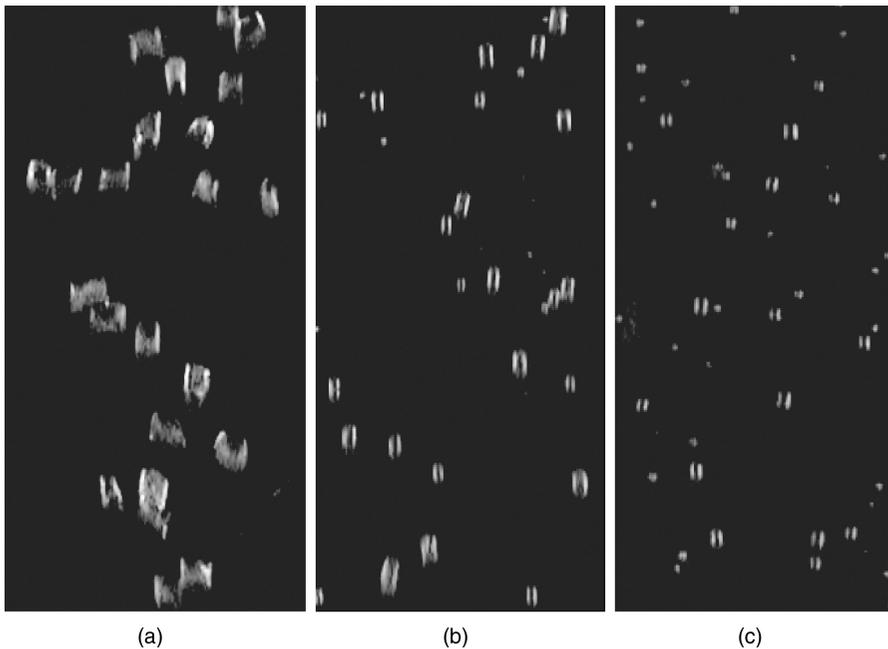
### VISUAL OBSERVATIONS

The images obtained for this gas-liquid system reveal that the bubble size is not constant throughout the column, the size being larger at the bottom of the column. This can be observed in Figures 2 and 3 for a DEA concentration of 1.0 M, and a gas flow rate of 20 L/h. Moreover, in the same gas-liquid system, the bubble size changes with the time in the middle and top sections of the column. This is due to the fact that the absorption process of carbon dioxide in aqueous diethanolamine solutions is associated with a moderately fast chemical reaction; therefore, the amount of carbon dioxide absorbed changes with the time as the reaction passes.

The photographs provide a visualization, according to column height, of the bubble size observed in the bubble column. The bubbles have a symmetric ellipsoidal shape. They rise almost vertically with the same speed without coalescence, drifting an amount of liquid to the top of the column. As described by other authors [8], the amount of liquid carried up by the bubbles, on its way down, hinders the uprising bubbles, thus resulting in an increase of gas holdup.

Comparing both figures, it can be observed that the bubble size does not change significantly with the time at the bottom of the column, while in the middle and in the top the bubble size increases during the process. However, until the saturation is reached, this system has higher interfacial area values at the top of the column. When the process finishes, bubble size is practically the same in the entire column.

As the process begins, the bubble size increases until it reaches a peak value, leveling off thereafter. This effect is more important at the top of the column, and less so at the bottom. Also, the effect increases with the amine concentration, and varies with the gas flow rate, depending on the flow regime.



**Figure 2.** Images of the bubbles at the beginning of the process for a concentration of 1.0 M and a gas flow rate of 20 L/h at different heights: (a) 20 cm, (b) 45 cm, and (c) 85 cm

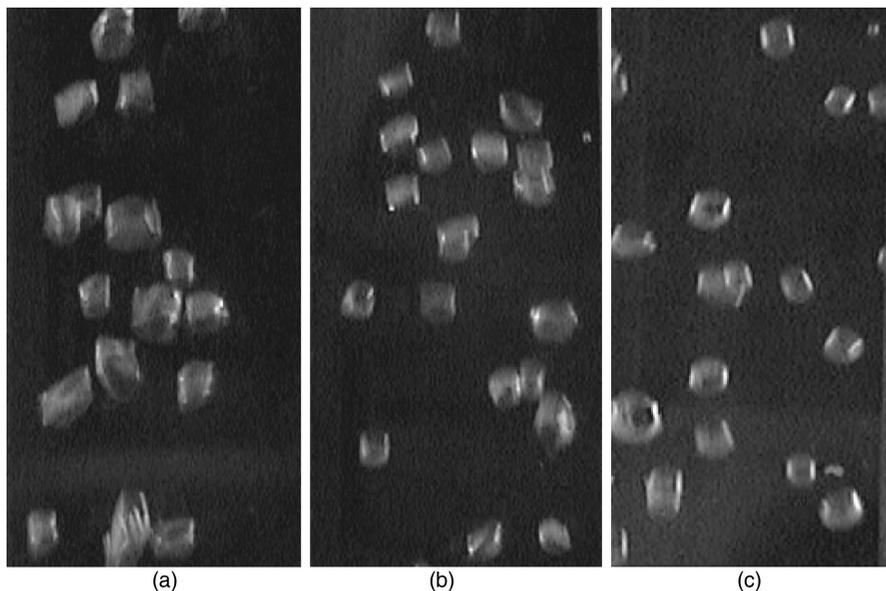
#### FLOW REGIME

Depending on the gas flow rate, the flow regimes observed in bubble column are the homogeneous bubbly regime encountered at low gas velocities, the heterogeneous (churn-turbulent flow) regime observed at higher velocities or in a transition regimen between the homogeneous and the heterogeneous [8].

The flow regimes can be distinguished by plotting the average gas holdup ( $\varepsilon$ ) versus the gas flow rate ( $q_G$ ). Hence, the gas holdup was measured using the volume expansion method which consists of measuring the volume change between the beginning of the experiment and the end.

$$\varepsilon = \frac{\Delta V}{\Delta V + V_L}$$

where  $V_L$  is the ungasged liquid volume and  $\Delta V$  is the volume expansion after gas dispersion, calculated from the liquid level change and the cross sectional area. In the



**Figure 3.** Images of the bubbles at the end of the process for a concentration of 1.0 M and a gas flow rate of 20 L/h at different heights: (a) 20 cm, (b) 45 cm, and (c) 85 cm

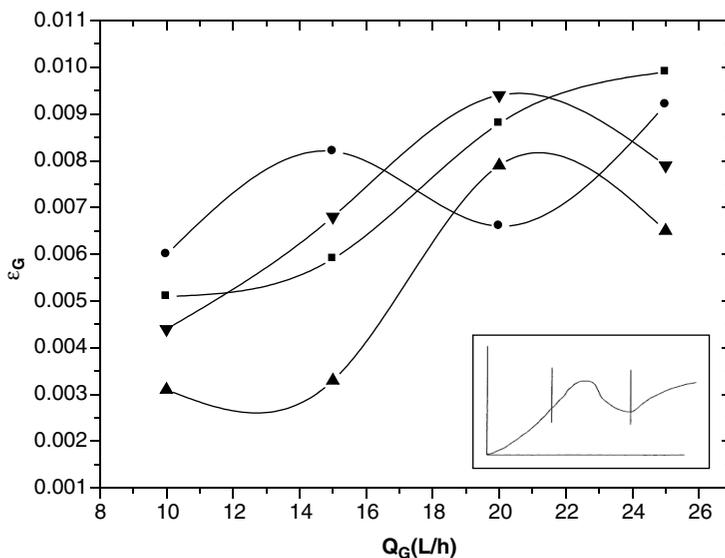
bubble column contactor, since the section is constant, the gas holdup is simply given by

$$\varepsilon = \frac{\Delta H}{\Delta H + H_L}$$

where  $H_L$  is the ungasged liquid height and  $\Delta H$  is the increase in liquid level after gassing.

Figure 4 shows the dependence of the gas holdup on the corresponding gas flow rate for all systems studied. A typical flow regime map [8] is also included for comparison. In this map, the first part of the curve corresponds to the homogeneous regime where the gas holdup increases with the gas flow rate. A transition regime follows, where a slight decrease in gas holdup is observed. Finally, in the heterogeneous regime the gas holdup continues to increase but with a lower slope than the homogeneous regime.

In the graphic, it is observed that, at lowest DEA concentration (0.05 M), the regime is always homogeneous with the operative gas flow rate. As the DEA concentration increases to 0.1 M, the regime is homogeneous at the low operation gas flow rate, reaching a heterogeneous regime at the higher flow rate. Whereas at higher DEA concentrations (0.3 and 1.0 M) and at the operation gas flow rates, the heterogeneous regime is not reached.



**Figure 4.** Effect of DEA concentration on gas holdup: 0.05 M (■), 0.1 M (●), 0.3 M (▲) and 1.0 (▼)

### BUBBLE SIZE

In all experiments, bubble sizes were calculated at three distances above the sparger surface (i.e., 20, 45 and 85 cm). Their values were permitted to obtain the interfacial area. The bubble shape was assumed to be oblate ellipsoidal, and the major and minor axes of the projected ellipsoid were measured using *UTHSCSA Image Tool* software.

The equivalent diameter of a sphere with the same volume as the ellipsoid was taken as the representative bubble dimension:

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

where  $E$  and  $e$  are, respectively, the major and minor axes of the ellipsoid in a two-dimensional projection. The bubble size distribution was defined by the Sauter mean diameter [9]:

$$d_{32} = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2}$$

where  $n_i$  is the number of bubbles having an equivalent diameter  $d_i$ .

It is expected that the mean bubble size increases with increasing gas flow rate, but this only occurs in the homogeneous regime. When the diethanolamine concentration is 0.1, the

bubble size increases at low gas flow (10 and 15 L/h) and decreases at high gas flow (20 and 25 L/h). At a concentration of 0.05 M, the bubble size increases with the gas flow rate.

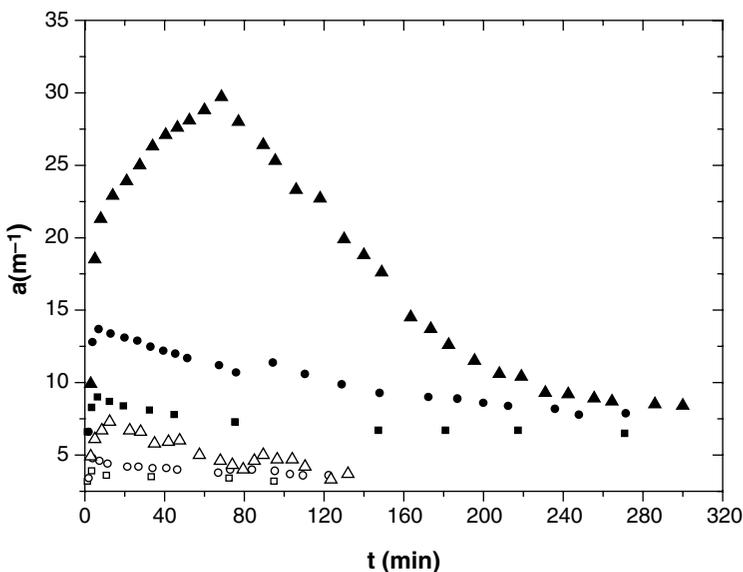
### INTERFACIAL AREA

The optimum operating conditions of a bubble column would be the ones which enhance mass transfer. This is accomplished by maximizing the gas-liquid interfacial area, a measure of which is given by

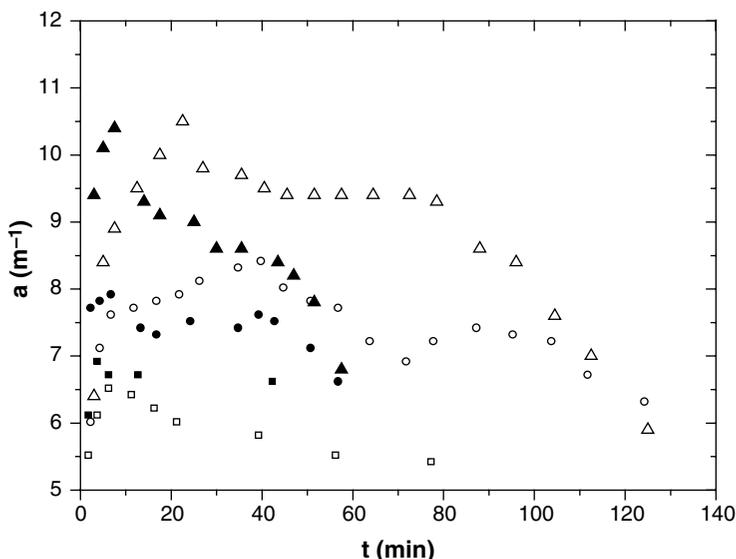
$$a = \frac{6\varepsilon}{d_{32}(1 - \varepsilon)}$$

where  $\varepsilon$  is the gas holdup and  $d_{32}$  the mean Sauter diameter. Consequently, the homogeneous bubbly flow regime encountered at the lower gas flow rates is the most desirable for mass transfer operations. By allowing, a large gas holdup value accompanied by relatively bubble size, it provides a greater interfacial area.

The interfacial area was calculated at three distances above the sparger surface. In Figure 5 the variation of the interfacial area with the operation time is presented for two



**Figure 5.** Effect of the column height and concentration of DEA on interfacial area ( $q_G = 15$  L/h): [DEA] = 0.3 M:  $h = 20$  cm ( $\square$ ),  $h = 45$  cm ( $\circ$ ),  $h = 85$  cm ( $\Delta$ ); [DEA] = 1.0 M:  $h = 20$  cm ( $\blacksquare$ ),  $h = 45$  cm ( $\bullet$ ),  $h = 85$  cm ( $\blacktriangle$ )



**Figure 6.** Effect of the column height and gas flow rate on interfacial area ( $[DEA] = 0.1 \text{ M}$ ):  $q_G = 10 \text{ L/h}$ :  $h = 20 \text{ cm}$  ( $\square$ ),  $h = 45 \text{ cm}$  ( $\circ$ ),  $h = 85 \text{ cm}$  ( $\Delta$ ),  $q_G = 20 \text{ L/h}$   $h = 20 \text{ cm}$  ( $\blacksquare$ ),  $h = 45 \text{ cm}$  ( $\bullet$ ),  $h = 85 \text{ cm}$  ( $\blacktriangle$ )

different amine concentrations, and for three distances. It can be observed that higher interfacial area values are reached when the DEA concentration increases. In both cases, it seems that at 85 cm there is a great variation in interfacial area, and it is obvious that the form of the curve changes with height. In simpler systems, like air-water, there is no variation with the height [10,11].

The interfacial area also changes with the gas flow rate (Figure 6). Higher values of interfacial area are obtained with lower gas flow rates. It can be attributed to the flow regime. In this case, at a gas flow rate of 10 L/h we have a homogeneous regime, while at 25 L/h we have a transition regime.

In all cases, the curves suggest that the majority of the bubbles have the same size near the sparger. Upon detaching from the sparger surface, however, the bubbles do not retain their initial size. This is attributable to the chemical reaction that seems to commence on the sparger surface.

## CONCLUSIONS

In bubble column reactor design, the homogeneous flow regime is usually the most desirable because it enhances the efficiency of the equipment by providing a greater gas-liquid interfacial area.

New data concerning average gas holdup values, Sauter diameters and interfacial area values are given for aqueous diethanolamine solutions. The data covers a range of concentrations and gas flow rates at different bubble column heights. It was found that the interfacial area depends on the amine concentration and gas flow rate, and is affected by the column height. The bubbles are greater at the bottom than at the top.

Finally, the interfacial area varies with time. This change is more important in the central and high zones of the column than at the bottom.

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