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Removal process of CO_2 using MDEA aqueous solutions in a bubble column reactor

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ABSTRACT

Present work analyses the behaviour and mass transfer of *N*-methyldiethanolamine (MDEA) in the removal process of carbon dioxide using a bubble column reactor (BCR) as gas–liquid contactor. The use of this type of equipment requires the interfacial area determination for the following mass transfer coefficient calculation based on absorption kinetics. In this work, a photographic method based on the bubble diameter determination, has been employed. The effect of contactor, operation conditions, liquid-phase nature and chemical reaction upon the mass transfer coefficient and interfacial areas have been analysed.

1. Introduction

The emission of carbon dioxide to atmospheric medium is principal cause of the global climate change and then a principal contributor to the greenhouse effect causing the global warming. Nowadays the technology employed to remove carbon dioxide are absorption/desorption processes employing chemical or physical absorption. Specifically in chemical absorption the reaction between carbon dioxide previously absorbed with alkanolamines (monoethanolamine (MEA) and diethanolamine (DEA)) is the most currently employed technology. In particular aqueous solutions of monoethanolamine have been extensively employed because of their high reactivity, low cost and low absorption of hydrocarbons [1].

In general, the reaction between CO_2 and primary and secondary alkanolamines in aqueous solutions is described by the zwitterion mechanism reintroduced by Danckwerts [2]. According to this mechanism, the primary and secondary alkanolamines react directly and reversibly with CO_2 to form a zwitterion intermediate, which is deprotonated by the bases existing in solution including alkanolamines, OH^- ions, and water to produce a stable carbamate and a protonated base, except for the CO_2–MEA reaction, which is independent of the concentration of OH^- ions [2–5].

Certain authors revealed that the addition of tertiary amines with primary or secondary amines presents certain advantages to increase CO_2 absorption capacity [6]. In contrast to primary and secondary amines, the tertiary amines do not react directly with CO_2 to form stable carbamates. Specifically, *N*-methyldiethanolamine (MDEA) seems a very good amine to get the previously commented characteristics.

For the reaction of CO_2 with tertiary alkanolamines, Donaldson and Nguyen [7] proposed the following reaction mechanism: this reaction mechanism is essentially a base-catalyzed hydration of CO_2, and the mechanism implies that tertiary amines cannot react directly with CO_2. In most of the literature on CO_2 kinetics with tertiary amines in aqueous solutions, it is assumed that reaction of CO_2 with MDEA is a pseudo-first-order reaction [3,8,9].

In this work we analyse the direct use of MDEA aqueous solutions as absorbent liquid-phase to remove carbon dioxide when a bubble column is employed as contactor. The bubble size distribution has been determined to obtain the interfacial area that allows the calculation of mass transfer coefficient.

2. Experimental

Aqueous solutions employed as liquid absorbent phases have been produced using different quantities of MDEA supplied by Aldrich (CAS number 105-59-9). The solutions were prepared by mass using a balance with a precision of $\pm 10^{-7}$ kg. To prepare the absorbent phases (in the range 0–1 mol L^{-1}), bi-distilled water has been employed.

All experiments were performed at room temperature, operating in batches with respect to the liquid phase. The bubble column is made of methacrylate, 1.03 m height, and has a square cross-section

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Nomenclature

a	specific interfacial area ($m^2\ m^{-3}$)
A	interfacial area (m^2)
C_A	carbon dioxide concentration ($mol\ dm^{-3}$)
C_B	MDEA concentration ($mol\ dm^{-3}$)
C_{B0}	initial MDEA concentration ($mol\ dm^{-3}$)
C_A^*	carbon dioxide solubility ($mol\ dm^{-3}$)
d	equivalent sphere diameter (m)
d_{32}	Sauter mean diameter (m)
D_A	carbon dioxide diffusivity ($m^2\ s^{-1}$)
e	minor axis of the projected ellipsoid (m)
E	major axis of the projected ellipsoid (m) or enhancement factor
Ha	Hatta number
k_2	rate constant ($m^3\ mol^{-1}\ s^{-1}$)
k_L	liquid mass transfer coefficient ($m\ s^{-1}$)
n	number of bubbles
N	absorption rate ($mol\ m^{-3}\ s^{-1}$)
Q_g	gas flow-rate ($L\ h^{-1}$)
t	operation time (s)
V	ungassed liquid volume (m^3)
ΔV	volume expansion (m^3)
x_B	MDEA molar fraction
Greek symbols	
ε_G	gas hold-up
η	liquid-phase viscosity (mPa s)
σ	liquid-phase surface tension ($mN\ m^{-1}$)

(side length 6 cm). For the injection and uniform distribution of the gas phase, a gas sparger (three glass capillary sparger) is installed at the centre of the bottom plate. The simplicity of the gas sparger produces a small dead zone near to the gas inlet.

The absorption process has been carried out at 25 °C using a similar experimental set-up employed by our research team in previous studies [10]. The gas to be absorbed, carbon dioxide, was passed through two bubbling flasks 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 bubbling flasks. The gas flow-rate fed to contactor was controlled with a mass flow controller (5850 Brooks Instruments) and measured with a soap flow-meter. The mass flow controller employed in the present study was calibrated by the supplier for the used gas flow-rates and pressure ranges. The gas flow-rates employed have been included into 15–30 $L\ h^{-1}$. The outlet gas flow-rate has been measured using a soap gas flow-meter and gas absorption rate was calculated as the difference between inflow and outflow rates.

The use of a BCR to analyse carefully the experimental results implies the knowledge of the interface area employed in the gas–liquid mass transfer. For this reason the present paper includes the determination of the interfacial area to the operation conditions under which the mass transfer experiments have been carried out. The methodology employed implies the use of a rectangular bubble column.

The bubble diameter was measured using a photographic method based on taking images of the bubbles along the height of the column and 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 different liquid phases employed (different concentration of MDEA), and for each gas flow-rate, which has been used. We used the Image Tool v2.0 software to carry out the necessary measurements of the geometric characteristics of the bubbles. Photographs of different bubble column zones were analysed, taking into account the possible influence of mass transfer accompanying of chemical reaction upon the bubble size along the liquid phase height.

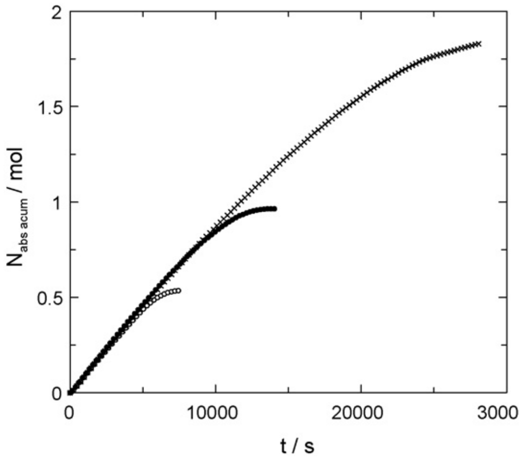

Fig. 1. Effect of initial MDEA concentration in liquid phase upon absorption process. (○) $C_{B0} = 0.25\ mol\ L^{-1}$. (●) $C_{B0} = 0.5\ mol\ L^{-1}$. (×) $C_{B0} = 1\ mol\ L^{-1}$. Gas flow-rate $Q_g = 15\ L\ h^{-1}$.

3. Results and discussion

In this work, different experiments of carbon dioxide absorption have been carried out in several aqueous solutions of MDEA varying the amine concentration in the liquid phase and the gas flow-rate of carbon dioxide fed to the bubble column reactor. In relation to the influence of liquid-phase composition (respect to MDEA concentration), the experimental results of absorption kinetics are shown in Fig. 1 at a fixed value of gas flow-rate.

Fig. 1 shows experimental data related with the carbon dioxide removed from the gas stream introduced in the gas–liquid reactor when the MDEA concentration is increased in the liquid phase. When the highest quantity of reactive (amine) is present in the liquid phase, a major quantity of carbon dioxide absorbed in the liquid phase reacts with amine.

On the other hand the experimental results shown in Fig. 1 indicate that at an operation time about 500 s (before liquid-phase saturation) the absorption rate is similar for the three solutions employed. This result indicates that the effect produced increases the amine (MDEA) concentration in the liquid phase is only the increment in global carbon dioxide removed but has no influence upon the speed of gas-phase absorption. This behaviour could be due to the low absorption step in relation to the chemical reaction between carbon dioxide and MDEA step.

Other important factor analysed in the present work was the influence of the gas flow-rate fed to the gas–liquid contactor and examples of the experimental results obtained for these kinds of experiments are shown in Fig. 2. In this figure the data indicates that the use of a higher carbon dioxide flow-rate produces a more quick exhaustion of the MDEA present in the aqueous solution media due to the absorption accompanying with chemical reaction. Fig. 2 shows that the removal process of the absorbed carbon dioxide with chemical reaction with MDEA is carried out until the amine is consumed observing that when the process reaches this exhaustion the quantity of carbon dioxide absorbed remain constant, without chemical or physical absorption.

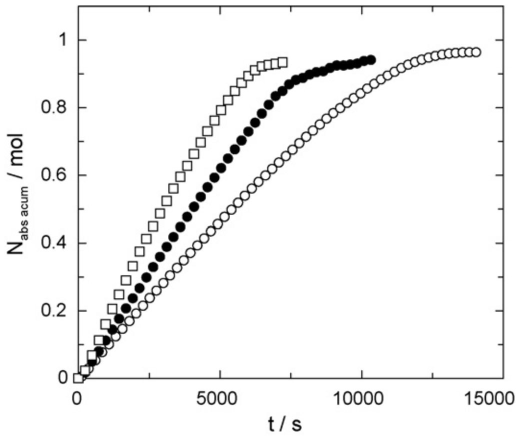

Fig. 2. Influence of gas flow-rate fed to the bubble column reactor. $C_{B0} = 0.5\ mol\ L^{-1}$. (○) $Q_g = 15\ L\ h^{-1}$. (●) $Q_g = 20\ L\ h^{-1}$. (□) $Q_g = 30\ L\ h^{-1}$.

In a previous paper, Camacho et al. [11] developed several studies to determine the kinetic behaviour corresponding to the reaction between carbon dioxide absorbed in aqueous solutions of MDEA. The studies of these authors indicate that the global process of absorption accompanying with chemical reaction is included in the fast reactions on the basis of the well-known classifications based on Hatta number values ($0.3 < Ha < 3.0$).

Using these previous results, we have developed a carbon dioxide removal process using these aqueous solutions of MDEA employing a bubble column reactor described in Section 2 (*vide supra*) to put in contact to the gas and liquid phases.

Due to the mass transfer process is the slowest step of the global process, is necessary to study the carbon dioxide transport to the liquid phase. The enhancement factor depends on the value of the mass transfer coefficient in absence of chemical reaction, the amine concentration, diffusivity of the reactants in the liquid phase and the values for the kinetic constants for the reactions evolved in the global process. Under certain conditions, the amine concentration at gas–liquid interface could be the same that in the liquid bulk and the reaction could be carried out completely at interface.

$$N = C_A^* a \sqrt{D_A k_2 C_B^{bulk}} \qquad (1)$$

where N, is the absorption rate of carbon dioxide, C_A^* and D_A, the solubility and diffusivity of carbon dioxide in the aqueous phase, a, is the interface area, k_2, the rate constant for the reaction between carbon dioxide and hydroxyl ions and C_B^{bulk}, the MDEA concentration in the bulk of the aqueous phase.

The use of this expression (Eq. (1)) needs that the concentration of amine remains constant practically along the time [12]. If this condition is not satisfied implies that a part of the chemical reaction between carbon dioxide and hydroxyl ions is carried out at interface and the other part in the bulk of the liquid. The surface renewal theory developed by Dankwerts contributed the expression shown in Eq. (2):

$$N = C_{CO_2}^* a \sqrt{D_A k_2 C_B^{bulk} + k_L^2} \qquad (2)$$

The use of Eq. (2) for fitting experimental data to mass transfer coefficient calculation implies the knowledge of specific area value under the different operation conditions. Specific area determination could be determined employing Eq. (1) but the conditions of application are not satisfied under the operation conditions. For this reason, another methodology must be applied for specific area determination.

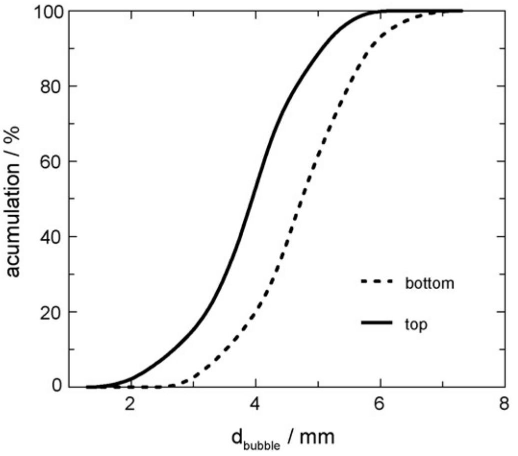

Fig. 3. Bubbles size distribution obtained at different column zones. $C_{B0} = 0.5\ mol\ L^{-1}$. $Q_g = 30\ L\ h^{-1}$.

The interfacial area in gas–liquid contactors is commonly determined using physical or chemical methods. In relation to physical methods, the photographic one is the most employed methodology. In relation to the chemical method, it is based on absorption measurements of a chemical absorption process with a well-known reaction kinetic. Due to the kinetic of the chemical absorption of carbon dioxide in aqueous solutions of MDEA has been determined in a previous paper, and in the basis of the equations previously commented, the interfacial area could be calculated. The knowledge of the interfacial area is necessary for the posterior mass transfer coefficient determination.

The images we obtained of the bubbles in the liquids employed show an ellipsoid shape. For this reason, major (E) and minor (e) axes of the projected ellipsoid (in two dimensions) was determined. The diameter of the equivalent sphere (Eq. (3)) was taken as the representative bubble dimension:

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

Different authors recommend using the Sauter mean diameter (d_{32}) [13], which is possible to determine using the data 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 which 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) [14]:

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

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.

An example of the experimental results obtained in this study is shown in Fig. 3. In Section 2, the method indicates that the bubble column must be analysed along the equipment height because

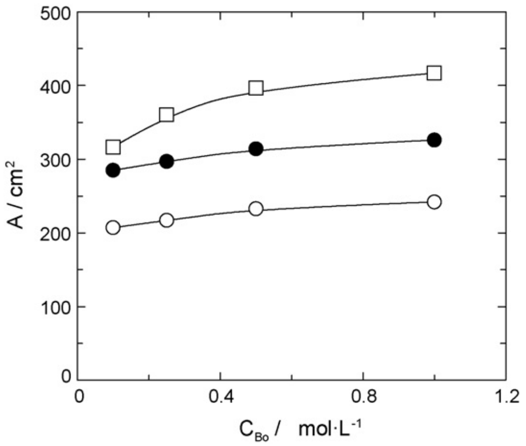

Fig. 4. Effect of amine concentration and gas flow-rate upon the interfacial area. (○) $Q_g = 15\,L\,h^{-1}$. (●) $Q_g = 20\,L\,h^{-1}$. (□) $Q_g = 30\,L\,h^{-1}$.

bubble size distribution could vary significantly along the bubble column due to the absorption process that carry out into the contactor.

Fig. 3 shows that this hypothesis must be taken into account because a clear difference in the bubble size distribution exists at the bottom and the top of the bubble column reactor. Smaller bubbles were detected at the top of the contactor respect the bubbles present at bottom zone. These size bubbles decrease is principally due to the transfer of gas carbon dioxide to the liquid phase.

Using Eqs. (4) and (5) and experimental data of bubble diameter in the different sections of contactor, it is possible to determine the area between both phases (gas and liquid) and analyse the influence of amine initial concentration and gas flow-rate on the generated interfacial area in the bubble column reactor. Fig. 4 shows the influence of both operational variables upon the value of interfacial area. An increase in the gas flow-rate produces a clear increase in the value of interfacial area. This behaviour is due to the increment in the gas hold-up because a higher volume of gas phase is introduced in the contactor. On the other hand, bubble diameter increases but it has negative effect on the interfacial area value.

An increase in the initial amine concentration in the liquid phase produces also an increase in the value of the interfacial area. This behaviour is assigned to the influence of surface tension of liquid phase upon the diameter of bubbles generated in this liquid phase. Experimental data shown in Fig. 5 indicates that the presence of MDEA in aqueous media produces a clear decrease in the value of surface tension. Different authors have studied the influence of this physical property on the hydrodynamics of bubble contactors [15,16] and they have concluded that a decrease in the surface tension produces a reduction in the bubbles size and it inhibits the coalescence phenomenon.

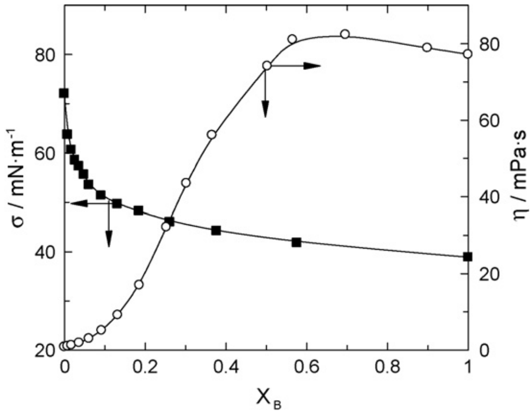

Fig. 5. Dynamic viscosity and surface tension of aqueous solutions of MDEA at 25 °C.

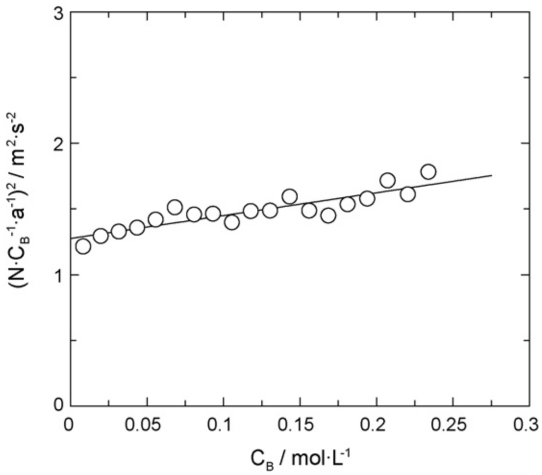

Fig. 6. Mass transfer coefficient determination employing Eq. (2). $Q_g = 15\,L\,h^{-1}$. $C_{B0} = 0.25\,mol\,L^{-1}$.

The experimental data corresponding to interfacial area under the experimental conditions employed in present work is employed in the mass transfer coefficient using Eq. (2) by fitting absorption intensity and amine concentration data. An example of the Eq. (2) application to the experimental data is shown in Fig. 6 obtaining the mass transfer coefficient by the square root of intercept.

The calculated results obtained for the mass transfer coefficient and the influence of initial MDEA concentration and gas flow-rate, are shown in Fig. 7. This figure shows that a higher initial concentration of amine produces an increase in the mass transfer coefficient until maximum because higher values of amine concentration produce a slight decrease in this coefficient. The decrease is due to the viscosity of the liquid phase that increases with the amine concentration (see Fig. 5). The influence of this physical property upon the mass transfer coefficient have been commented widely by different authors [15,16].

The calculated values of mass transfer coefficient have been employed to calculate the enhancement factor of this system to analyse also the effect of viscosity upon the global mass transfer

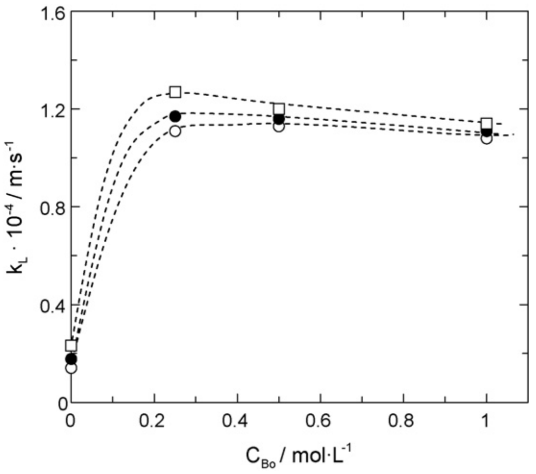

Fig. 7. Influence of initial MDEA concentration and gas flow-rate on mass transfer coefficient. (○) $Q_g = 15\,L\,h^{-1}$. (●) $Q_g = 20\,L\,h^{-1}$. (□) $Q_g = 30\,L\,h^{-1}$.

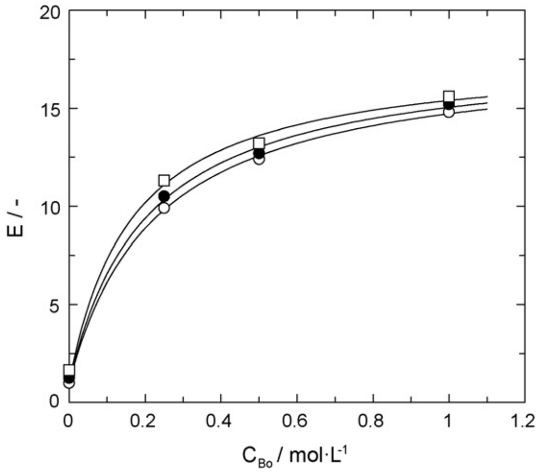

Fig. 8. Influence of initial MDEA concentration and gas flow-rate on enhancement factor. (○) $Q_g = 15\,\mathrm{L\,h^{-1}}$. (●) $Q_g = 20\,\mathrm{L\,h^{-1}}$. (□) $Q_g = 30\,\mathrm{L\,h^{-1}}$.

coefficient. The enhancement factor has been calculated as the relation between the mass transfer coefficient data shown in Fig. 7 and the corresponding coefficient in absence of chemical reaction. This coefficient determined without chemical reaction has been determined by absorption experiments similar than previous ones commented but with the addition of HCl to the liquid phase (aqueous solutions of MDEA) with the aim to obtain acidic solutions that inhibit the chemical reaction between carbon dioxide and amine [17]. The obtained results for enhancement factor are shown in Fig. 8 and it shows that the enhancement factor increases continuously when the initial amine concentration increases in the liquid phase.

4. Conclusion

The studies developed in present work allow to conclude that the bubble diameter and interfacial area in bubble contactor is importantly influenced by the gas flow-rate and amine concentration. Both parameters produce an increase in the interfacial area. The bubble diameter decreases considerably as long as the bubbles ascend along the bubble contactor.

The interfacial area data was employed to calculate the mass transfer coefficient that is influenced by the gas flow-rate and initial amine concentration, producing both parameters an increase in the coefficient value. An increase in the amine concentration produces a continuous increase in the enhancement factor.

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