AQUEOUS SOLUTIONS OF PYRROLIDINE FOR CARBON DIOXIDE CAPTURE

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Abstract
Present study analyses absorption process with chemical reaction between carbon dioxide and aqueous solutions of pyrrolidine. The determination of kinetic has been carried out in order to determine the regime of process, and then the process has been performed in a bubble column reactor and the rate of capture of acidic gases has been analyzed.

Keywords: absorption, carbon dioxide, pyrrolidine, bubble column, reaction

1. Introduction

Fossil fuel combustion from power plants or refineries is one of the most important sources of carbon dioxide emission[1]. Several technologies are available to reduce the carbon dioxide emission from industrial gas streams, but chemical absorption with alkanolamines (i.e. monoethanolamine -MEA-, diethanolamine –DEA-, di-2-propanolamine –DIPA-, triethanolamine –TEA-, and methyldiethanolamine -MDEA), is the most used for low to moderate carbon dioxide partial pressures[2,3]. This method is efficient and usually permits removal high percentage of carbon dioxide emitted.

In general, the reaction between CO_2 and primary and secondary alkanolamines in aqueous solutions is described by the zwitterion mechanism reintroduced by Danckwerts[1]. 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[2, 3].

In this work we analyse the direct use of pyrrolidine aqueous solutions as absorbent liquid phase to remove carbon dioxide when a bubble column is employed as gas-liquid contactor. The first step of the experimental work consists in reaction kinetics determination corresponding to the reaction between carbon dioxide and pyrrolidine. The experimental work to obtain information about reaction kinetics was conducted in a stirred cell having a planar interfacial area working in batches with respect to both phases (gas and liquid).

The experimental studies related with the absorption with chemical reaction in a bubble column reactor show very interesting results of mass transfer rate of carbon dioxide from gas to liquid phase. An increase in the pyrrolidine concentration in the liquid phase, and also an increase in the gas flow rate, produces a clear increase in the value of carbon dioxide mass transfer rate.

2. Experimental section

The gas-liquid kinetic experiments were conducted in an experimental set-up employed previously[4] consisted on a stirred cell having a planar interfacial area working in batches as regards both phases. Four baffles have been placed in its internal wall to improve the mixing and prevent vortex formation during stirring. The gas to be absorbed, carbon dioxide, was passed through two humidifiers 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". A soap flow-meter was used to determine the absorption rate of carbon dioxide by the absorption accompanying the chemical reaction produced by the amine present in the liquid phase. The absorption rate was measured by analysing the movement (produced by the consumption of carbon dioxide) of the soap film along the calibrated glass tube. The absorption processes have been carried out at different temperatures (7 to 55 ºC) by connection of humidifiers, stirred cell and flow-meter to a thermostat-cryostat.

The absorption process has been carried out at 25 ⁰C using a similar experimental set-up employed by our research team in previous studies (see figure 1). The gas to be absorbed, carbon dioxide, was passed through two bubbling flasks at 25 ⁰C 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 pressures 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.
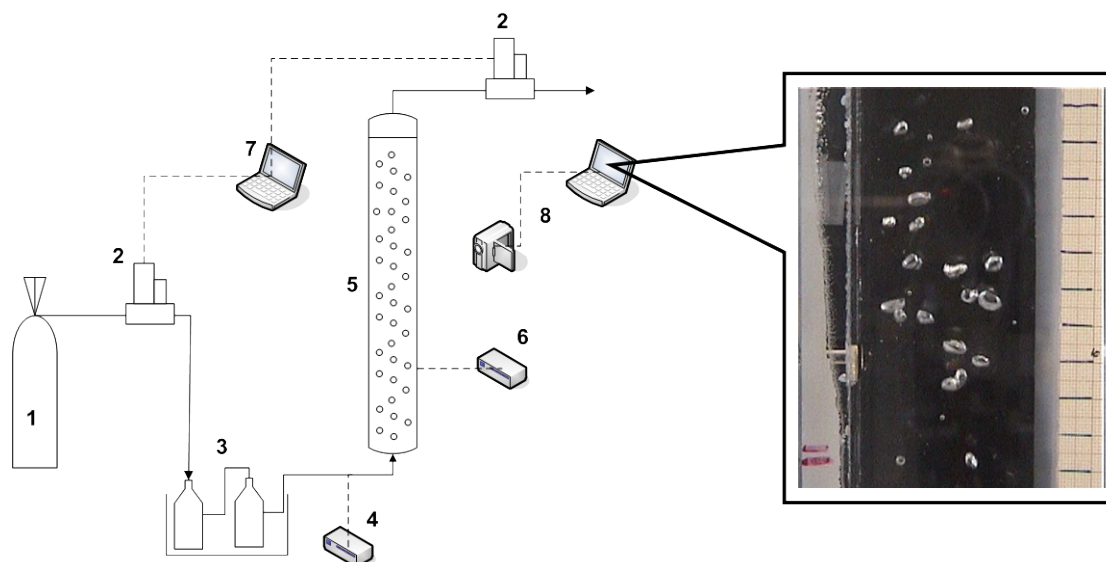
Figure 1. Experimental set-up employed in carbon dioxide absorption experiments. (1) Gas cylinder; (2) Mass flowmeter/controller; (3) Humidifier and thermostatic bath; (4) Pressure gauge; (5) Bubble column reactor; (6) Temperature gauge; (7) Flow data recorder; (8) Setup for interfacial area determination.

3. Results and discussion

3.1 Kinetics and absorption regime

Carbon dioxide flow density was determined by means of experimental data corresponding to the absorbed quantity of carbon dioxide along the operation time. Figure 2 shows the experimental results which were obtained in relation to the carbon dioxide flux density determined for the different liquid phases and experimental conditions employed in this work. In this figure, experimental data shows a linear trend, and this behaviour allows the use of this experimental data for kinetic determination. The value of the slope of the linear plot allows the calculation of the absorption volumetric flux at different operation conditions, show in figure 3.

Using the experimental data of carbon dioxide absorbed volume along the operation time, the gas flow density has been determined under the different experimental conditions. Figure 3 shows the results calculated for the experimental system employed in present work. Also in this figure is possible observes the influence of amine concentration in the liquid phase and the effect caused by temperature upon the carbon dioxide absorption rate. The behaviour observed for the carbon dioxide – amine system shows a positive effect upon absorption rate when the amine concentration increases in the liquid phase. Also the influence of temperature was the same producing an increase in the gas mass transfer rate.

It has been shown in the literature [5] that the partial order with respect to CO_2 is always 1, as we obtained in this work based on the experimental data, but the partial order with respect to the amine can vary between 1 and 2 depending on the chosen amine[6].

$$N_A = C_{Ao}\sqrt{D_A \cdot k_{1,n} \cdot C_{Bo}^{n}} \tag{1}$$

where C_{Ao} and C_{Bo} are the initial concentrations of carbon dioxide and glucosamine in the liquid phase, D_A is the gas diffusivity in glucosamine aqueous solutions and $k_{1,n}$ is the overall reaction rate constant.
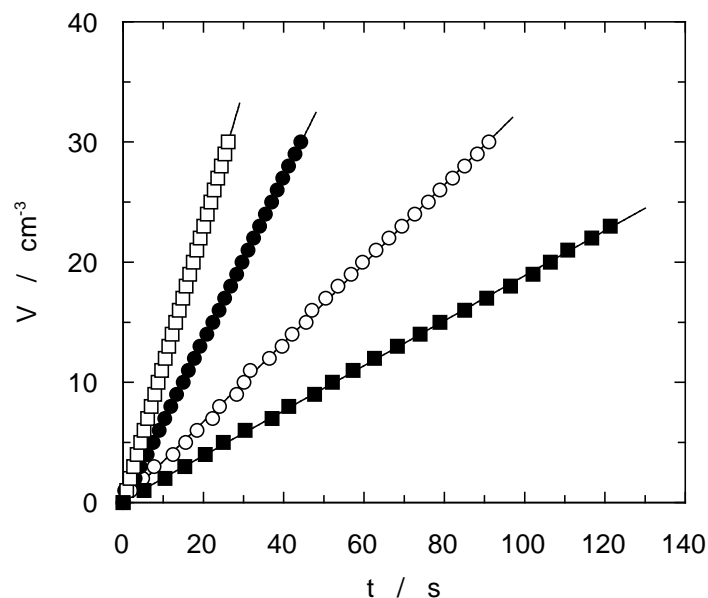
Figure 2. Influence of composition upon absorption rate of carbon dioxide in aqueous solutions of pyrrolidine. (■) $C_B = 0.1$ mol·L^{-1}; (○) $C_B = 0.3$ mol·L^{-1}; (●) $C_B = 0.4$ mol·L^{-1}; (□) $C_B = 0.5$ mol·L^{-1}. T = 25 ºC.
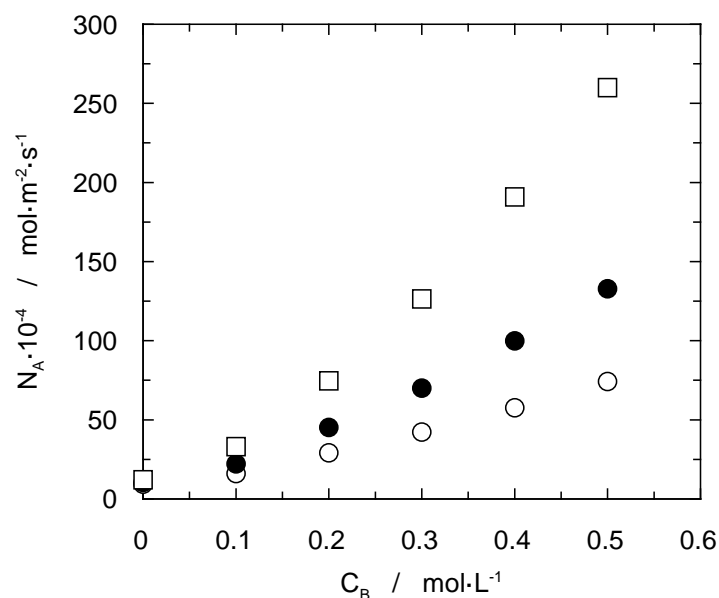
Figure 3. Influence of pyrrolidine concentration upon the carbon dioxide flow. (○) T = 15 ºC; (●)T = 35 ºC; (□) T = 55 ºC

The initial carbon dioxide concentration in the liquid phase coincides with the concentration in equilibrium in gas phase and this parameter could be replaced in equation 1 employing Henry's law. These considerations allow us to obtain the linearized expression shown in equation 2 to fit experimental data as well as to calculate the reaction order corresponding to amines:

$$\log\left(\frac{N_A^2 \cdot He^2}{P_A^2 \cdot D_A}\right) = \log(k_{1,n}) + n \cdot \log(C_{Bo}) \tag{2}$$

where He is Henry's constant and P_A is the carbon dioxide partial pressure. Fitting the experimental values corresponding to carbon dioxide flow density *versus* the initial amine concentration the fit agreement is satisfactory and then, kinetic parameters were determined. In relation to the reaction order, it shows a medium value of 2.1 for pyrrolidine. In a great part of carbon dioxide – aqueous solutions of amines systems the corresponding reaction order is one [7], but in certain systems[8] the same reaction order that in present work, was obtained.

Also, in present work the value of the kinetic constant corresponding to each experimental system has been determined using equation 2. The calculated values for this parameter and the influence of temperature upon this value, are shown in figure 6. For low temperature, both systems takes similar values for the kinetic constant but when temperature increases, the carbon dioxide – pyrrolidine system takes high values for this parameter in relation with the other system.

The influence of temperature upon the value of the kinetic constant for the reaction studied in the present work has been analyzed. Experimental values have been fitted using an Arrhenius type equation to calculate the pre-exponential factor and the activation energy. Equations 4 and 5 show the calculated values for both parameters.

$$\ln k = 37.9 - \frac{9620}{T} \tag{3}$$

3.2 Absorption process in bubble column reactor
As it has been commented in the experimental section, a bubble column has been used to perform the absorption process with chemical reaction between carbon dioxide and aqueous solutions of pyrrolidine. For that, different experimental conditions have been used (gas flow-rate and concentration of amine in liquid phase). In figure 4, as an example, an experiment where the evolution of gas-flow rate measured in the out with time is shown, and the comparison with behaviour obtained for the flow transferred to liquid phase, where chemical reaction takes place a different behaviour has been observed with regard to what was observed by other researchers for amine based systems. As carbon dioxide is transferred to liquid phase, amine is consumed and therefore, the gas transfer rate to liquid phase decreases. This behaviour would be expected for a quite conventional system, but in this case, it is observed that for a moment, transfer rate of gas towards liquid phase stops its decrease and a stretch with a quite constant absorption rate is observed. This constant absorption remains an important part of the experiment. When this stage has concluded, a decrease for the gas flow-rate absorbed is observed until absorption rate gets to zero value, and therefore, out gas flow-rate is equal to in one. This process is due to disappearance of reagent in liquid phase which is necessary for chemical reaction takes place and physical saturation of liquid phase with carbon dioxide.

The behavior shown in figure 4 has been similar to the behavior obtained for experiments in which liquid phases with different amine concentrations have been used, as it can be observed in figure 5. When concentration of amine in liquid phase is lower, period of time with constant absorption rate is lower, and it is practically inexistent for the lowest amine concentration and gas flow-rate fed to the reactor.

The same as for out gas flow-rate, pH has been registered through the time, in order to obtain more conclusions about reactive process which is happening within the liquid phase. As it can be observed in figure 5, although a plane area which coincides with the stretch of constant absorption rate is not observed, the tendency obtained shows a reduction in the rate of fall of pH through the time.
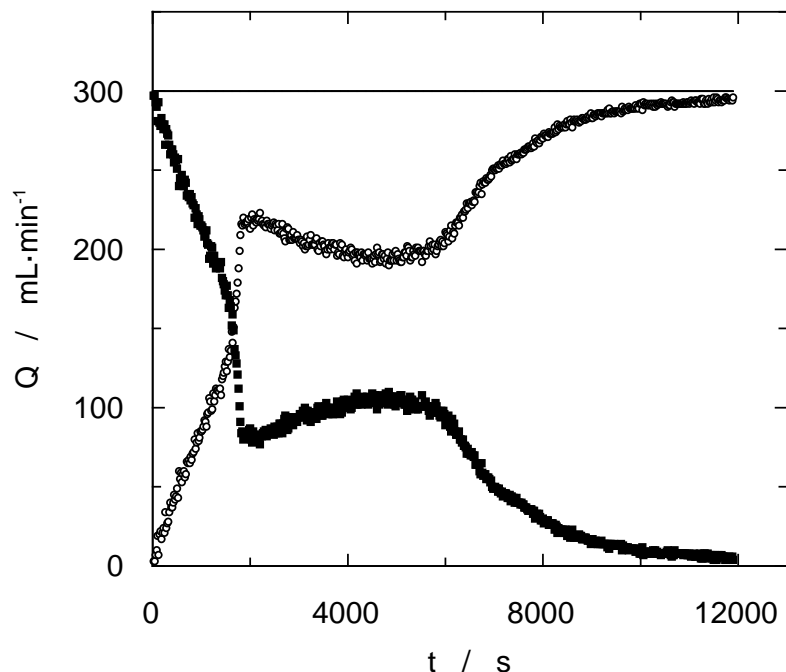
Figure 4. Temporal evolution of outlet and absorbed carbon dioxide flow-rates. ($\bigcirc$) Outlet flow-rate, ($\blacksquare$) Absorbed flow-rate. Solid line corresponds to inlet gas flow-rate. $C_B = 0.2$ mol·L^{-1}. $Q_g = 18$ L·h^{-1}.
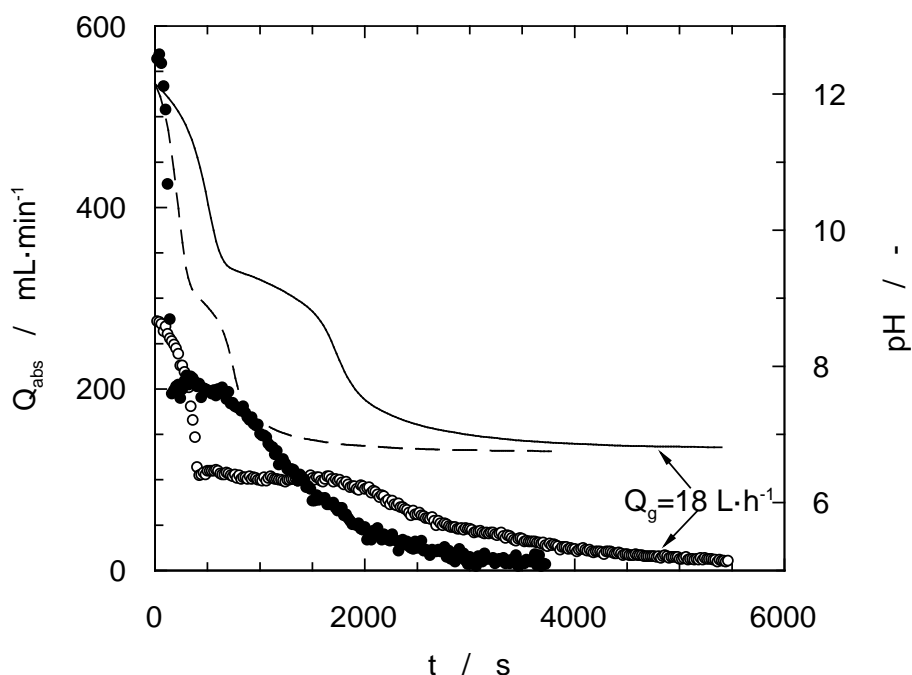
Figure 5. Influence of gas flow-rate upon the absorption rate and pH evolution. ($\bigcirc$) and solid line correspond to $Q_g = 18$ L·h^{-1}. ($\bullet$) and dashed line correspond to $Q_g = 40$ L·h^{-1}.

Hence, probably a reaction which avoids the acidification of liquid phase exists, and due to reactions and compounds present in this type of absorption with chemical reaction between carbon dioxide and amines, the reaction of bicarbonate ion to produce carbonate ion takes special importance, forming a regulator solution which attenuates the reduction of pH. Then, mechanisms that several researchers have proposed[9] are shown below.

$$2\ RNH + CO_2 + H_2O \leftrightarrows RNCO_2^- + RNH_2^+ + H_2O \tag{4}$$

$$2\ RNH + CO_2 + H_2O \leftrightarrows RNH_2 + HCO_3^- + RNH \tag{5}$$

$$HCO_3^- \leftrightarrows CO_3^- + H^+ \tag{6}$$

Based on the conclusions reached by Park et al[9], when steric hindered amines are used, like pyrrolidine, formation of carbamate ion (equation 4) loss importance with regard to the formation of bicarbonate ion (equation 5) as the quantity of carbon dioxide transferred to liquid phase increases. This last reaction allows the stechiometric between reagents (carbone dioxide and pyrrolidine) to be 1:1, and the quantity of carbon dioxide which can be absorbed increases. On the other hand, bicarbonate ion reacts to produce carbonate ion (equation 6), which promotes the reaction between carbon dioxide and pyrrolidine and tampon solution is formed to keep pH of liquid phase constant and in applicable range of tampon carbonate-bicarbonate.

4. Conclusions

Kinetic studies of chemical reaction produced into liquid phase between carbon dioxide and pyrrolidine has shown that the global regimen is instantaneous, what makes the system appropriate to capture carbon dioxide in an efficient way. The order of reaction with respect to CO_2 has been one and two with respect to pyrrolidine.

The application of this system to capture carbon dioxide in a bubble contactor shows an intermediate area with absorption rate constant, assigned to the preference of reaction to produce bicarbonate ion, and prevent the formation of carbamate ion. This mechanism makes the capture of carbon dioxide more effective.

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