

CO₂ Capture by Pyrrolidine: Reaction Mechanism and Mass Transfer

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DOI 10.1002/aic.14343

Published online January 13, 2014 in Wiley Online Library (wileyonlinelibrary.com)

A new carbon dioxide capture process by means of gas–liquid absorption using pyrrolidine aqueous solutions in a bubble column reactor obtaining suitable results in comparison with other commonly used amines is analyzed. The influence of several operation variables such as amine concentration and gas flow rate has been studied. Carbon dioxide mass-transfer rate data have shown a different behavior than other amine-based systems because a constant value in absorption rate was observed in the middle of batch experiments. ¹³C and ¹H NMR spectroscopy studies were performed to analyze the species present during the experiments. These data and the carbon dioxide loading allowed to explain the reaction mechanism existed between these reagents. © 2014 American Institute of Chemical Engineers AIChE J, 60: 1098–1106, 2014
Keywords: capture, absorption, NMR, bubble column, carbamate, bicarbonate

Introduction

The fossil fuel combustion from power plants or refineries is one of the most important sources of carbon dioxide emissions.¹ Several technologies are available to reduce the carbon dioxide emission from industrial gas streams, but the chemical absorption with alkanolamines is the most widely used methodology.^{2,3} This method is efficient and it usually allows the removal of a high percentage of the emitted carbon dioxide. Previous studies concluded that primary and secondary alkanolamines react, directly and reversibly, to the carbon dioxide by forming a zwitterion intermediate, which is deprotonated by the bases present in the solution to form carbamate.^{4,5} The formation of the carbamate increases the reaction rate, but usually limits the loading to 0.5 mol of carbon dioxide/mol of amine.⁶ By contrast, tertiary amines do not react directly to the carbon dioxide to form carbamate. Generally, this kind of amine reacts slower than primary and secondary amines.⁷ Conversely, the formation of bicarbonate is usually attributed to tertiary amines, but previous studies indicate that this reaction can also take place with primary and secondary amines.⁸ Figure 1 shows the mechanism proposed by Park et al.¹⁰ for the chemical absorption of carbon dioxide in primary amines. This reaction mechanism indicates that the weight of carbamate or bicarbonate production has high importance upon carbon dioxide loading in the liquid phase. This fact is due to the different stoichiometry of each reaction. In the reaction to produce bicarbonate, a

higher amount of amine remains free (CO₂:amine = 1:1) and available to react with carbon dioxide. This pathway causes a significant increase in carbon dioxide loading in comparison with the another mechanism (carbamate production) which have a CO₂:amine = 1:2 stoichiometry.¹¹ Besides these two reaction paths, it is necessary to take into account that the produced carbamate can suffer an hydrolysis reaction producing bicarbonate and free amine. This kind of reaction depends on different variables such as amine concentration, liquid phase pH, and carbamate stability.^{12,13}

The sterically hindered amines have been proposed in the last years as suitable alternatives to be used in carbon dioxide capture. However, different discrepancies were observed about the carbon dioxide loading reached by this kind of systems.⁹ This behavior can be explained on the basis of a decrease in carbamate stability for this kind of amines.¹⁴

These studies (the relation between absorption rate and speciation during chemical absorption) are necessary to evaluate the aptitudes of amines to be used in carbon dioxide capture processes. The main part of the previous studies has only analyzed the absorption rate^{1,5,6,8} but a complete characterization of the process is needed. The carbon dioxide absorption rate, the chemical reaction rate, the carbon dioxide loading (and the relation with reaction mechanism), and the ratio between carbon dioxide and amine concentration at the beginning of the process, can play a very important role in the election of a specific process. This choice allows to decrease the size of the equipment and then the use of a lower amount of liquid phase to reach the same carbon dioxide capture. Also, the process footprint would decrease due to the reduction in energetic cost for absorption/regeneration cycles, because a minor liquid-phase volume must be treated.¹⁵ Present work uses pyrrolidine aqueous solutions

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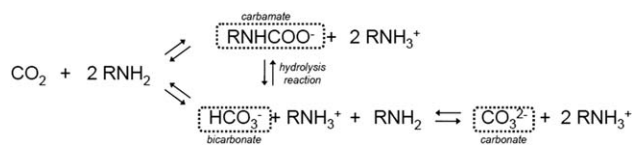


Figure 1. Reaction mechanism for carbon dioxide absorption in amine aqueous solution proposed by Park et al.⁹

due the good behavior of this amine based on a high reaction rate and a different reaction order in relation with amine concentration.¹⁶

Experimental Section

Commercial grade carbon dioxide of 99.998% purity, supplied by Carburos Metálicos, was used as gas phase in present work to be fed to gas–liquid contactor. Pyrrolidine of $\geq 99\%$ purity was obtained from Fluka. Aqueous solutions of this cyclic amine were prepared on mass with double distilled water.

Carbon dioxide mass transfer to liquid phases studies have been carried out using a bubble column contactor similar to other used in previous studies¹⁷ and it has been deeply described. The gas–liquid contactor used in these studies was a square bubble column reactor ($6 \times 6 \times 110 \text{ cm}^3$) with a liquid volume of 3 L built in methacrylate. The carbon dioxide stream was put in contact with water at 25°C to saturate the gas phase, and then to remove the water transfer from liquid phase to gas one. The inlet and outlet gas flow rates were controlled and measured with two mass flow controllers (Alicat Scientific). The mass flow controllers were calibrated by the supplier for the experimental conditions used in this work. The working regime was continuous in relation to the gas phase and batch regarding the absorbent liquid one. Liquid phase temperature was measured at different column heights (23, 45, and 67 cm) during absorption experiments. Also, several thermograms were obtained using a FLIR ThermoCAM E300 from the beginning of the absorption experiments and these images were analyzed by FLIR ThermoCAM Reporter software. The outer superficial temperature over the stainless steel column was measured using Scotch 33 electrical tape with a known emissivity. This bubble column reactor has the same geometrical characteristics than the previously commented one but it was made in stainless steel.

^1H and ^{13}C NMR spectroscopy was used to investigate qualitatively the solutions of pyrrolidine (concentration of solution between 0.1 and 0.5 mol L^{-1}) loaded with carbon dioxide in a capture process by means of chemical absorption. The MestReC 4.7 software package (MestreLab Research) was used for spectra processing. Spectra were acquired on 300 MHz Varian Mercury spectroscope. The samples of amine solution were taken from the middle zone of reactor system. Tetradeuterated methanol (CD_3OD) (TMS) was used as internal reference for the processing of ^{13}C NMR spectra.

Results and Discussion

In general,¹⁸ the chemical reaction mechanism corresponding to carbon dioxide + amine systems in the liquid phase involves the following reactions



Reactions (3) and (4) are considered instantaneous and reversible at equilibrium, in comparison with the other reactions shown previously.¹⁸ The commonly proposed mechanism for the reaction between carbon dioxide and different amines involves the formation of zwitterion ($\text{R}_2\text{NH}^+\text{COO}^-$) and the subsequent deprotonation of zwitterion by a base to produce carbamate (R_2NCOO^-) and protonated base (R_2NH_2^+), followed by carbamate reversion by hydrolysis.¹⁴ The choice of a zwitterion mechanism was considered suitable for modeling the absorption of carbon dioxide into aqueous solutions of different amines solutions.^{19,20}

Although the final product in different experimental systems is bicarbonate, the formation of a zwitterion could be the rate-determining step because the deprotonation involves only proton transfer and is considered to be very fast.^{21,22} Any base present in the solution may contribute to the deprotonation of zwitterion. The contribution of each base would depend on its concentration as well as how strong a base is. Hence, the main contribution to the deprotonation of the zwitterion in this system would come from pyrrolidine and to a lesser extent from H_2O and OH^- . Moreover, it has been well recognized that the relative formation of carbamate anion and bicarbonate ion has a crucial effect on the carbon dioxide loading in aqueous alkanolamine solutions. The bicarbonate production mechanism causes the presence of a higher amount of free amine that is available to react with carbon dioxide molecules, which finally leads to a remarkable enhancement in the carbon dioxide loading. The overall reaction stoichiometry indicates that 2 mol of amine are required per mole of carbon dioxide reacted for the carbamate anion, whereas a one-to-one ratio is required for the bicarbonate ion.¹¹ The degree of hydrolysis of the carbamate anion is determined by reaction parameters such as the amine concentration, solution pH, and chemical stability of the carbamate anion.^{12,13,23} In a rich amine solution, the concentration of unreacted amine depends on the carbamate stability constant.



In this work, NMR spectroscopy was used to perform speciation studies through time during carbon dioxide absorption experiments in pyrrolidine aqueous solutions. NMR studies have started with ^1H and ^{13}C NMR spectra of pyrrolidine– H_2O system (Figure 2). Deuterium oxide (D_2O) was used as NMR solvent of the different pyrrolidine aqueous solutions. To have an internal reference to ^{13}C NMR, a drop of deuterated methanol has also added. The ^1H NMR of pyrrolidine aqueous solution shows two triplet groups of signals to 2.8 and 1.7 ppm corresponding to the α and β protons to nitrogen atom, respectively, and the ^{13}C NMR spectrum shows also two groups of signals to 46.4 and 25.6 ppm assigned to the equivalent carbons.

About bicarbonate–carbonate equilibrium (Eq. 4), a substantial discrepancy was observed in literature with regards to the chemical shift of these ions.^{24,25} In a previous work, fast proton exchange in the $\text{HCO}_3^-/\text{CO}_3^{2-}$ equilibrium was

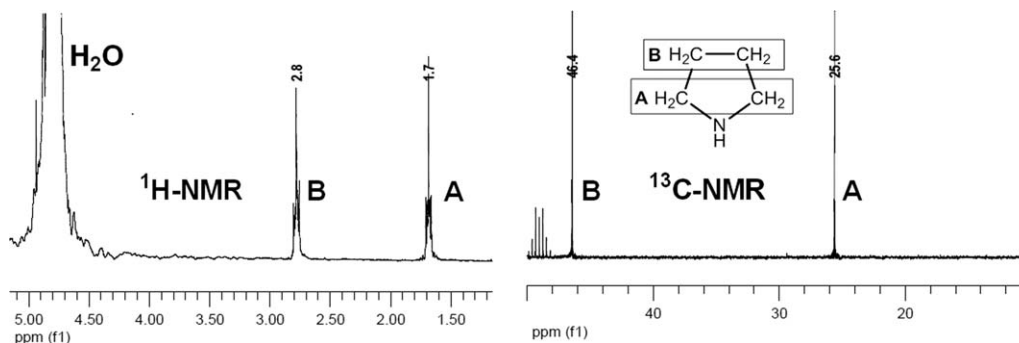


Figure 2. ^1H and ^{13}C NMR spectra of pyrrolidine- H_2O system at 293 K.

assigned to a ^{13}C NMR chemical shift in the range of $165 < \delta < 161$ ppm.²⁶ The chemical shift of CO_3^{2-} gives a signal to 168.7 ppm, whereas for HCO_3^- , it appears at 161.4 ppm. Mixtures of both substances give a chemical shift between both extremes.

Other interesting study consisted in the analysis of the chemical shifts corresponding to pyrrolidine carbons at different values of aqueous solutions pH. Different measurements were performed at several pH values: 10.4, 5.4, 3.1, and 1.6. The experimental data indicate that proton exchange is very fast and only one peak is observed for both compounds (amine and protonated amine). At basic medium, the signals corresponding to pyrrolidine carbons are present at 46.4 and 25.6 ppm. When the medium is acidified, a chemical shift in original peak at high field was observed from 25.6 to 24.5 ppm ($\Delta\delta = 1$ ppm).

These previous studies have allowed to obtain necessary information to analyze the NMR spectra obtained during the carbon dioxide chemical absorption in pyrrolidine aqueous solutions. Previous research works²⁷ have concluded that the nuclear magnetic resonance is a useful technique to analyze this kind of chemical absorption. These previous studies commonly analyze only the initial and final products of absorption process. Present work studies the temporal evolution of the species that exist in the liquid phase produced by the chemical reaction between carbon dioxide and pyrrolidine. This information can draw the preferential mechanism of chemical absorption. At initial time (see Figure 3), two different signals are observed that corresponds to the carbons of pyrrolidine. This spectrum unchanged during the initial period of experiment, although the chemical absorption between carbon dioxide and pyrrolidine is produced. It was confirmed by the change in outlet gas flow rate and bubbles size. This behavior is caused by the nonideality of the bubble column reactor. The chemical absorption between carbon dioxide and pyrrolidine shows a fast regime¹⁶ and it produces that bubbles practically disappear in the column bottom section. This fact causes a low liquid turbulence in the main part of the contactor. Taking into account that in bubble contactors the gas flow rate is the stirring agent, at initial experiment time the concentration of substances is not the same in each part of the reactor. The situation of sample port (placed in the middle height of bubble column) and the low turbulence at initial time explain the absence of changes in NMR spectra.

At t_3 , ^{13}C NMR spectrum (10 min) new peaks appear. The more interesting signals appear at low field: 168.8 and 164.1 ppm. These signals are assigned to the $\text{HCO}_3^-/\text{CO}_3^{2-}$ equilibrium (previously commented) and the formation of

pyrrolidine carbamate. The last product is also associated to signal duplication at high field. Two new peaks appear near to the original pure amine signals (46.4 and 25.6 ppm) caused by the presence of new species. The carbamate signal at 164.1 ppm is associated to the signals present at 47.1 and 26.1 ppm. The peaks at 46.4 and 25.3 ppm correspond to the amine/protonated amine equilibrium.

During the absorption experiment, the signal at 168.8 ppm (in the t_3 spectrum) assigned to carbonate/bicarbonate equilibrium shifts to low field: 168.0 ppm (t_6), 166.0 ppm (t_8), 164.1 ppm (t_9), 162.4 ppm (t_{10}), 161.4 ppm (t_{14}), and 161.3 ppm (t_{18}). At initial experiment time, the carbonate/

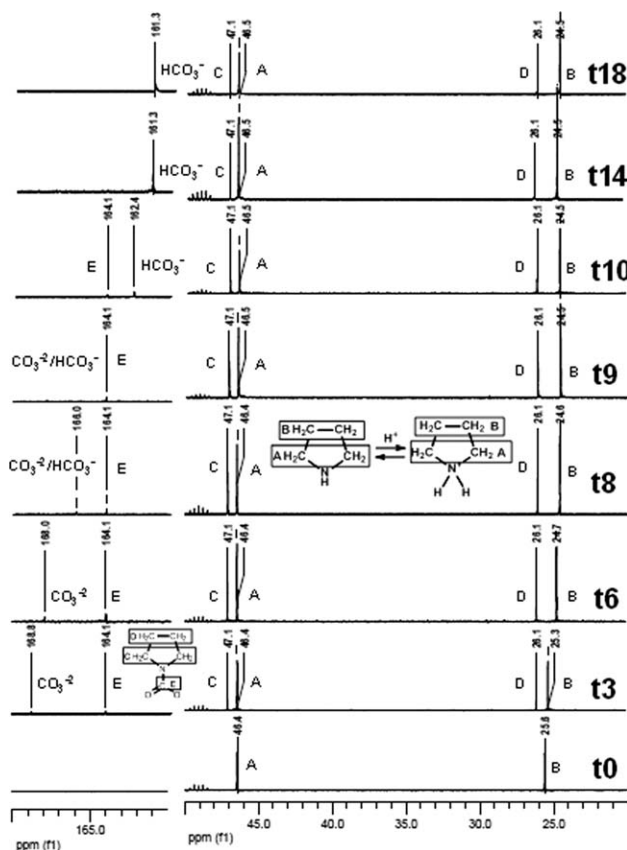


Figure 3. ^{13}C NMR spectra corresponding to carbon dioxide absorption in pyrrolidine aqueous solutions.

$C_{\text{PYR}} = 0.3 \text{ mol L}^{-1}$ and $Q_g = 18 \text{ L h}^{-1}$ ($t_0 = 0$ min; $t_3 = 10$ min; $t_6 = 25$ min; $t_8 = 35$ min; $t_9 = 45$ min; $t_{10} = 65$ min; $t_{14} = 140$ min; and $t_{18} = 325$ min).

bicarbonate equilibrium is completely shifted to carbonate ion but at the end of the absorption experiment only exists the bicarbonate ion. In the same way, the amine/protonated amine equilibrium shifts to the second one substance from 25.3 ppm (*t*3) to 24.5 (*t*18). This signal is in agreement with the previously obtained value of pyrrolidine in acidic medium. Since *t*8, a significant decrease in carbamate signals is observed and these peaks disappear at *t*14 time.

The observed behavior differs significantly in relation with previous studies using another secondary amine (diethanolamine)²⁷ because the production of carbamate is observed until carbon dioxide loading is near to 0.5 mol CO₂·mol amine⁻¹. Then, the presence of bicarbonate increases in the liquid phase due to carbamate hydrolysis. The main differences between both systems (diethanolamine and pyrrolidine aqueous solutions) are: (1) the existence of the bicarbonate/carbonate equilibrium from the beginning of the absorption experiment and (2) the low carbamate stability that causes the total disappearance of this compound and the end of experiments. For other amine-based systems (e.g., with monoethanolamine or diethanolamine), the presence of bicarbonate and carbonate is observed at high carbon dioxide loadings. This fact is related with the carbamate stability and the structure of pyrrolidine (sterically hindered compound) causes a reduction in stability and then the reaction mechanism produces an increase in carbon dioxide loading. This behavior can increase the interest of pyrrolidine for its use in carbon dioxide capture. The presence of bicarbonate at low carbon dioxide loading produces positive effect upon reaction stoichiometry and then an increase in capture capacity.

Speciation studies in carbon dioxide absorption experiments have also been performed using ¹H NMR. Zero time spectrum shows two signal groups corresponding to protons of α carbon (2.8 ppm) and protons of β carbon to nitrogen (1.7 ppm). In the first two samples (*t*1 = 2 min and *t*2 = 5 min), no changes in the spectrum was observed for the same reason than the perviously commented one for ¹³C NMR spectra (nonideal mixing into the bubble contactor at the beginning of the experiment).

The spectrum corresponding to *t*3 shows the formation of two new signal groups that appears as triplets at 3.2 and 1.85 ppm. These signals are assigned to the formation of carbamate molecule. Conversely, a chemical shift of initial signals to low field is observed. The triplet at 1.7 ppm moves slightly to 1.8 ppm, and the other one at 2.8 ppm moves to 2.9 ppm. These movements are caused by the equilibrium between the amine and the conjugated acid. This signal group continues changing their chemical shift to low field during the absorption experiment caused by the amine ↔ protonated amine is displaced to the last one. In the six sample (*t*6), the spectrum shows these two group signals at 2.0 and 3.2 ppm and also, the presence of carbamate signal at 1.8 ppm (protons of β-carbon) as a triplet. Along the absorption experiment, the carbamate signal (1.85 ppm) decrease its intensity until dissapear. All these experimental results confirm the previous conclusions obtained using the ¹³C NMR spectra.

Similar absorption experiments have been carried out under different conditions (amine initial concentration and gas flow rate), and ¹H and ¹³C NMR analysis were performed using samples obtained during these experiments. The obtained results confirm the previous conclusions reached for 0.3 mol L⁻¹ pyrrolidine aqueous solutions (Figures 3 and 4). Taking

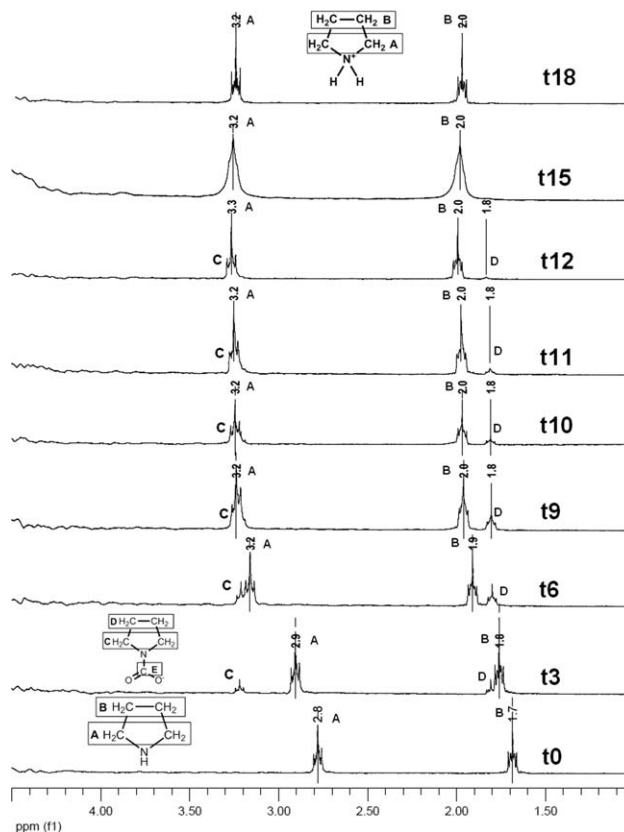


Figure 4. ¹H NMR spectrum corresponding to the chemical absorption of carbon dioxide in aqueous solution of pyrrolidine.

*C*_{PYR} = 0.3 mol L⁻¹ and *Q*_g = 18 L h⁻¹ (*t*0 = 0 min; *t*3 = 10 min; *t*6 = 25 min; *t*9 = 45 min; *t*10 = 65 min; *t*11 = 85 min; *t*12 = 100 min; *t*15 = 165 min; and *t*18 = 325 min). The peaks legend corresponds to the molecular structures shown in Figure 3.

into account the lowest concentration solution (0.1 mol L⁻¹) the spectra at different times show only the presence of peaks corresponding to bicarbonate (160.2 ppm) and protonated amine (23.5 and 45.5 ppm). The absence of signals corresponding to other species, such as carbamate and carbonate, is due to the low amine concentration in the liquid phase. Then, the experiment with the lowest amine concentration is similar than the final experimental zone in the previously analyzed system (0.3 mol L⁻¹).

Conversely, experiments using the highest amine concentration (see Figure 5) in the liquid phase show a similar peaks time evolution than experimental data obtained for 0.3 mol L⁻¹ pyrrolidine aqueous solution. At low time, the presence of carbamate, carbonate–bicarbonate equilibrium, and amine–protonated amine equilibrium is confirmed by the NMR signals. The same behavior than previous one for 0.3 mol L⁻¹ aqueous solution is observed: (1) the shift of carbonate–bicarbonate equilibrium peak to 160.2 ppm, corresponding to bicarbonate and (2) the initial presence of carbamate signals that disappear when pyrrolidine concentration decreases. When a high amine concentration is used, the presence of carbamate is observed during more time.

In relation with absorption kinetics, aqueous solutions of pyrrolidine have shown a suitable behavior to be used for carbon dioxide capture by means of chemical absorption.¹⁶ This good result is due to the high reaction rate between

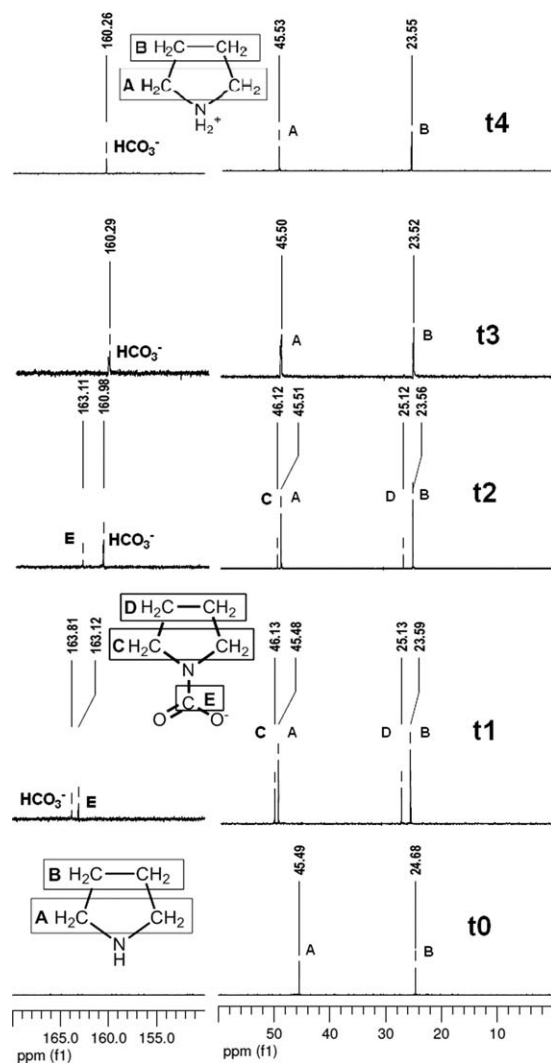


Figure 5. ^{13}C NMR spectrum corresponding to the chemical absorption of carbon dioxide in aqueous solution of pyrrolidine.

$C_{\text{PYR}} = 0.5 \text{ mol L}^{-1}$, $Q_g = 40 \text{ L h}^{-1}$ ($t_0 = 0 \text{ min}$; $t_1 = 45 \text{ min}$; $t_2 = 90 \text{ min}$; $t_3 = 135 \text{ min}$; and $t_4 = 180 \text{ min}$). The peaks legend corresponds to the molecular structures shown in Figure 3.

loaded carbon dioxide and pyrrolidine in comparison with other amines.^{28,29} Taking this as starting point, the absorption in a bubble column reactor has been performed under different experimental conditions to analyze the behavior of this kind of aqueous solutions for carbon dioxide capture. An example of the experimental data corresponding to absorption experiments are shown in Figure 6. On the basis of these experimental data, it is possible to calculate the amount of carbon dioxide transferred to the liquid phase. These data show a different behavior in comparison with the corresponding ones for other amines aqueous solutions. A decrease in absorption rate is observed when operation time increases until this variable reaches a plateau. The zone with a constant absorption rate is observed for an important period of time. After it, a decrease in the value of absorption rate is observed until the liquid phase saturation is reached, and the absorbed molar gas flow rate is zero.

The experimental data shown in Figures 6 and 7 have been obtained under different operation conditions (gas flow

rate and pyrrolidine concentration) and they allow to analyze carefully the absorption process with chemical reaction. Figure 6 also shows the experimental data obtained when different pyrrolidine initial concentration is used in the liquid phase. When pure water is used as liquid phase (in the absence of amine), the behavior is different because a monothonic decrease is observed (without the constant absorption rate zone). When pyrrolidine concentration increases in liquid phase, the presence of the plateau is observed increasing the length of this period when amine concentration increases. This fact is produced because an increase in amine concentration causes a large operation time. Also, a higher initial amine concentration produces an increase in the time needed to reach the constant absorption rate period. In relation with the influence of carbon dioxide flow rate (Figure 7) upon absorption rate, an important increase is observed when a higher gas flow rate is fed to the bubble column. This behavior is due to an increase in the value of gas–liquid interfacial area.³⁰ This enhancement in interfacial area increases carbon dioxide mass transfer that reacts with pyrrolidine in the liquid phase. This behavior shows that mass transfer is the rate-determining step in this process.

Other amines aqueous solutions show a different behavior than the observed for carbon dioxide–pyrrolidine system because a monothonic decrease in the value of absorption rate is observed until the saturation is reached.^{31–33} Conversely, results corresponding to monoethanolamine or 1-amino-2-propanol aqueous solutions produce certain similar behavior than the previously commented for pyrrolidine aqueous solutions: there is not a constant absorption rate period, but a change in the trend is observed.

On the basis of the absorption rate experimental data, it is possible to conclude that the chemical absorption process for this system takes place by a mechanism with certain differences with well-known systems. Constant absorption rate periods were observed for pseudo-first-order systems at initial time (when the reagent concentration is high). Under these conditions, the amine concentration could be considered “constant” that allows to maintain the absorption rate independent of time.

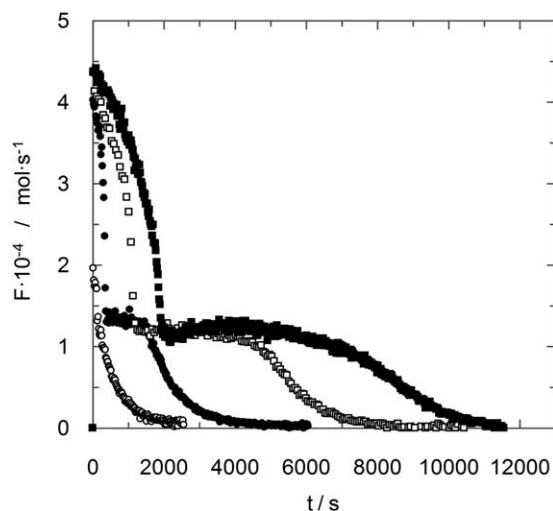


Figure 6. Effect of amine concentration upon carbon dioxide absorption rate in pyrrolidine aqueous solutions.

$Q_g = 40 \text{ L h}^{-1}$; (\circ) $C_{\text{PYR}} = 0 \text{ mol L}^{-1}$; (\bullet) $C_{\text{PYR}} = 0.1 \text{ mol L}^{-1}$; (\square) $C_{\text{PYR}} = 0.3 \text{ mol L}^{-1}$; and (\blacksquare) $C_{\text{PYR}} = 0.5 \text{ mol L}^{-1}$.

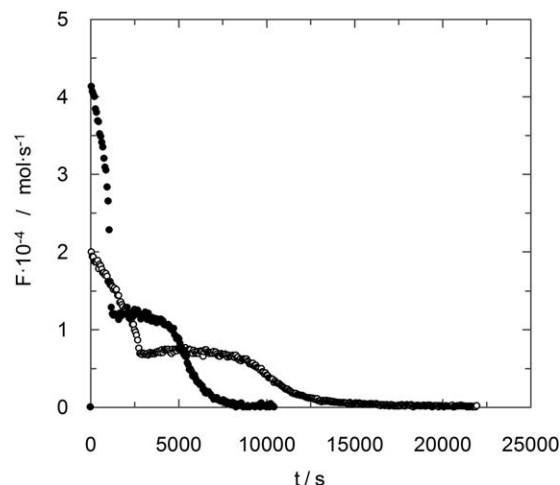


Figure 7. Influence of gas flow rate upon carbon dioxide absorption rate in pyrrolidine aqueous solutions.

$C_{\text{PYR}} = 0.3 \text{ mol L}^{-1}$; (○) $Q_g = 18 \text{ L h}^{-1}$; and (●) $Q_g = 40 \text{ L h}^{-1}$.

As previously commented, carbon dioxide chemical absorption in pyrrolidine aqueous solutions shows a different behavior in comparison with other amines. This behavior could be divided in three zones: the first and third zones involve a decrease in the value of mass-transfer rate, however, the second one shows a constant value. On the basis of NMR spectra, the products present in the liquid phase, in the first zone, are carbonate ion and carbamate. The basic pH of the liquid phase at the beginning of the experiment causes a complete shift in the bicarbonate/carbonate equilibrium to carbonate observing the ^{13}C signal corresponding to this equilibrium at a chemical shift near to 168 ppm. Also, these products are observed near to Zone 2 (constant mass-transfer rate period). At this moment, the peak corresponding to the carbonate–bicarbonate equilibrium begins to shift from the value of 168 ppm (corresponding to carbonate ion). This behavior indicates that in the first zone only carbonate ion exists but when amine concentration decreases (due to the chemical reaction with carbon dioxide) the equilibrium is moved to bicarbonate. This fact is produced because the liquid phase pH decreases and then the buffer reaction (bicarbonate/carbonate) is activated. Taking into account the Reaction (6), the hydrolysis of carbamate produces bicarbonate ion and free pyrrolidine. The hydrolysis reaction is enhanced in sterically hindered amines. This free amine would be used to react with carbon dioxide. Both reactions: (1) carbonate/bicarbonate buffer and (2) carbamate hydrolysis produce bicarbonate and free pyrrolidine. The production of free pyrrolidine molecules explains the constant mass-transfer rate zone with a similar behavior than a pseudo-first-order regime. Pyrrolidine reacts with carbon dioxide and decrease its concentration, but conversely, amine molecules are been produced by the buffer reaction and the hydrolysis of carbamate. This fact is supported by NMR spectra previously commented because carbamate peak tends to disappear with time by means of the hydrolysis reaction. The zone with the last decrease in mass-transfer rate corresponds mainly to physical absorption process when the chemical reaction has concluded. In this zone, only bicarbonate ion peak is observed in the NMR spectra.

Then, the behavior shown by pyrrolidine aqueous solutions is very interesting for its use in carbon dioxide separation by chemical absorption because the main product is bicarbonate, and this fact implies: (1) an increase in carbon dioxide loading that also increase the driving force and (2) a reduction in regeneration energetic costs because the amount of energy needed to produce the amine regeneration is lower when bicarbonate is the product than for carbamate pathway.³⁴ Then, both characteristics are suitable for a possible use at industrial level because pyrrolidine takes the best characteristics of secondary (high reaction rate) and tertiary amines (high carbon dioxide loading and lower energetic requirements for regeneration).

The reaction between carbon dioxide and pyrrolidine in aqueous solution is fast,¹⁶ and this characteristic implies that mass transfer process is the rate-limiting step. Under certain conditions, the amine concentration at the gas/liquid interface could be the same as in the liquid bulk, and the reaction could be carried out completely at the interface. Equation 1 must be used under these conditions

$$N = C_A^* \cdot a \cdot \sqrt{D_A \cdot k_2 \cdot C_B^{\text{bulk}}} \quad (7)$$

where N , is the carbon dioxide absorption rate, C_A^* and D_A , the solubility and diffusivity of carbon dioxide in the aqueous phase, a , is the gas–liquid interfacial area, k_2 , the rate constant for the reaction between carbon dioxide and pyrrolidine and C_B^{bulk} , the pyrrolidine concentration in the bulk of the aqueous phase.

The use of this expression (Eq. 1) needs a high amine concentration to remain practically constant throughout time.³⁵ If this condition is not satisfied, a part of the chemical reaction is carried out at the interface and the other part in the liquid bulk. The surface renewal theory developed by Danckwerts contributed the expression shown in Eq. 2

$$N = C_A^* \cdot a \cdot \sqrt{D_A \cdot k_2 \cdot C_B^{\text{bulk}} + k_L^2} \quad (8)$$

where k_L is the liquid side mass-transfer coefficient.

The use of Eq. 2 to fit the experimental data to calculate the mass-transfer coefficient implies the knowledge of the specific interfacial area value under the different operation conditions. These data have been obtained from a previous study²¹ which analyzed the hydrodynamic behavior in this experimental system.

Equation 2 uses the pyrrolidine concentration and this variable has been calculated by means of the amount of carbon dioxide absorbed through the experiment. The reaction stoichiometry is needed to calculate the mass-transfer coefficient. The first part of the absorption experiments (the first decrease zone in absorption rate) was used to perform the fit, the involved reactions use 2 mol of amine per mole of carbon dioxide. Taking into account this stoichiometry and using the values of absorption rate and gas–liquid specific interfacial area, the mass-transfer coefficient has been calculated. Figure 8 shows an example of this fitting procedure. A good agreement between the linear fit and the experimental data is observed. Also, Figure 8 shows the influence of pyrrolidine concentration. When amine concentration increases, a decrease in the value of intercept (square mass-transfer coefficient) is observed. The same procedure was used to fit all absorption rate experimental data, and then the value of mass-transfer coefficient upon the different experimental conditions was obtained (see Figure 9).

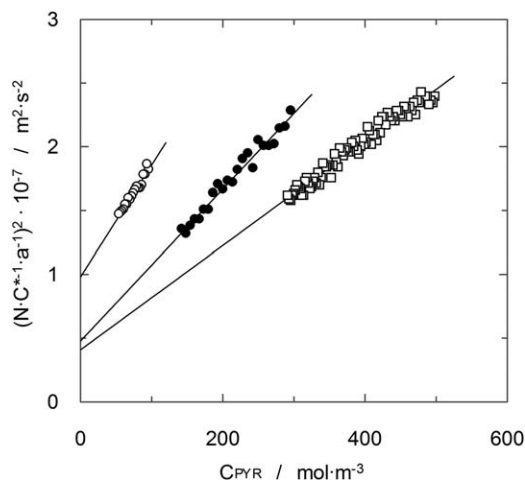


Figure 8. Mass-transfer coefficient determination for the system carbon dioxide–pyrrolidine.

$Q_g = 18 \text{ L h}^{-1}$; (○) $C_{PYR} = 0.1 \text{ mol L}^{-1}$; (●) $C_{PYR} = 0.3 \text{ mol L}^{-1}$; and (□) $C_{PYR} = 0.5 \text{ mol L}^{-1}$.

When gas flow rate increases, an increase in mass-transfer coefficient is observed too. This fact indicates that this variable (gas flow rate) has an important influence on gas–liquid interfacial area and upon the mass-transfer process.³¹ This is due to the fact that an increase in the gas flow rate fed to the bubble column produces also an increase in the power supplied to the liquid phase and, therefore, the turbulence in the liquid in the contactor increases as well. This increase also produces an enhancement in mass transfer in the liquid phase, avoiding concentration gradients and diffusional limitations. It is observed that higher differences regarding the gas flow rate influence are obtained for low amine concentration. However, at high concentrations of pyrrolidine in the liquid phase, a slight decrease in the value of the mass-transfer coefficients under different flow rates is observed. This behavior is related with the liquid phase viscosity, which is a very important physical property to analyze mass-transfer processes. At low pyrrolidine concentrations, viscosity increases slightly³⁶ and, therefore, an increase in the gas flow rate fed to the bubble column produces a significant

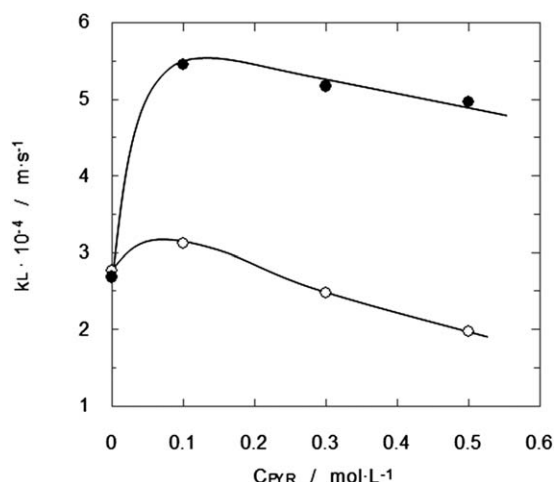


Figure 9. Pyrrolidine concentration influence upon mass-transfer coefficient.

(○) $Q_g = 18 \text{ L h}^{-1}$; (●) $Q_g = 40 \text{ L h}^{-1}$.

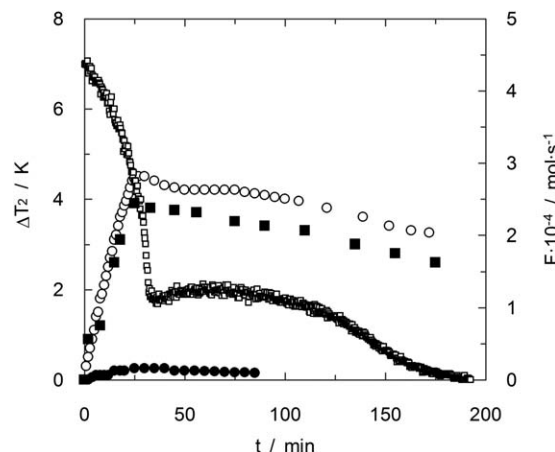


Figure 10. Liquid phase temperature during carbon dioxide chemical absorption in pyrrolidine aqueous solutions.

$Q_g = 18 \text{ L h}^{-1}$. Temperature data at 45 cm from bottom: (○) $C_{PYR} = 0.5 \text{ mol L}^{-1}$ (thermometer); (●) $C_{PYR} = 0.1 \text{ mol L}^{-1}$ (thermometer); and (■) $C_{PYR} = 0.5 \text{ mol L}^{-1}$ (thermographic camera). Absorption rate: (□) $C_{PYR} = 0.5 \text{ mol L}^{-1}$.

increase in turbulence. When amine concentration increases, the viscosity also increases significantly and then, the effect of gas flow rate over the turbulence decreases. A higher gas flow rate is necessary to produce the same degree of turbulence when a viscous liquid phase is used.

Regarding the influence of pyrrolidine concentration in the liquid phase upon the value of mass-transfer coefficient, a similar behavior than other carbon dioxide–amine systems^{31,32} was observed. When the amine concentration increases in the liquid phase, a significant increase in the mass-transfer coefficient is observed until a maximum is reached. Then, an increase of amine concentration produces a monothonic decrease in the coefficient value. The enhancement of mass transfer at low concentrations of pyrrolidine is due to the chemical reaction, which maintains the carbon dioxide concentration in the liquid phase low and, therefore, the driving force is kept high. However, in spite of increasing the amine concentration keeps the driving force high, a decrease in mass-transfer rate can be observed. The factor which causes this behavior is, as it was aforementioned, the viscosity of the liquid phase. This physical property plays a very important role in mass-transfer processes, having a negative effect.^{37,38} It introduces a greater resistance to the mass transfer, probably due to a lower renovation of liquid elements near interface. In this case, the liquid phase viscosity increases with pyrrolidine concentration, with a very negative influence upon mass-transfer rate, compensating the positive effect caused by the fast chemical reaction.

Also, different experiments were performed determining the liquid phase temperature throughout absorption experiments, and Figure 10 shows an example of the obtained results. In this reactor, there were not significant differences between each thermometer that indicates a suitable mixing into the reactor. For this reason, the data shown in Figure 10 only correspond to the thermometer placed in the middle position in the bubble column reactor. The highest change temperature was observed when the highest amine concentration was used. This fact is produced because the chemical reaction rate is higher than for the other experiments. The

behavior observed in Figure 10 shows an opposite trend than gas absorption rate. In the first part of the experiment, an increase in temperature was observed. It corresponds with the highest absorption rate caused by the production of carbamate. A previous study³³ concluded a different behavior using other amines. It observed that a high increase in temperature is observed in the middle of the experiment and a constant value was observed during the first part of the experiment. This behavior is caused by the thermometer position (in the top of the reactor). The main part of the absorption is produced in the lower part of the column and then the temperature of the upper part of the reactor remained constant.

After this first decrease in absorption rate, the reaction mechanism changes as previously commented, and the carbamate hydrolysis is produced. This fact causes a decrease in liquid phase temperature because it is an endothermic reaction. The experimental results corresponding to liquid phase temperature confirm the previously obtained reaction mechanism using pyrrolidine aqueous solutions by means of absorption rate and NMR spectra. Also, Figure 10 shows that a decrease in amine concentration causes an important decrease in the change of temperature.

The experimental results obtained by the thermometers and the reached conclusions have been confirmed using the data obtained using a thermographic camera (see Supporting Information Figure S1). The experimental results of the mean temperature show a similar behavior than previously commented by the first experimental technique. The values of changes in temperature are lower because the thermal conductivity of both materials (methacrylate and stainless steel) are different, and the studies using stainless steel column produce a higher heat-transfer rate and then the liquid temperature is lower than for experiments using the methacrylate column. The behavior is the same and confirms the presence of two different periods governed: the first one by the carbamate formation (exothermic reaction) and the second one by the carbamate hydrolysis (endothermic reaction).

The magnitude of the temperature changes in this study is not very large and for this reason it was not taken into account for mass-transfer coefficient determination. This conclusion was reached on the basis of a previous work³³ that did not observe significant differences in this coefficient using the experimental temperature profiles and an isothermal approximation.

Conclusions

Pyrrolidine aqueous solutions have shown a characteristic behavior including an important constant absorption rate period similar than the corresponding one for pseudo-first-order systems. This period and the reaction mechanism increase significantly the carbon dioxide loading. The analysis of this behavior was performed using ¹³C and ¹H NMR spectroscopy to evaluate the reaction products, and the production of carbonate and carbamate were observed at the beginning of experiments which indicates a 2:1 (amine:carbon dioxide) stoichiometry. When carbon dioxide loading increases, the carbamate stability decreases because the pyrrolidine is a sterically hindered amine, producing bicarbonate. It causes an increase in free amine concentration available to react with carbon dioxide. This released amine is produced during the constant absorption rate period. Then,

the final stoichiometry of the process is 1:1 that enhances the carbon dioxide capture capacity.

The results for liquid side mass-transfer coefficient indicate an enhancement of mass transfer at low amine concentration and a slight decrease when amine concentration is increased. The positive behavior can be caused by an increase in driving force due to the weight of each reaction caused by the molecule structure. This decrease is caused by the pyrrolidine accumulation at the interface due to the amphiphilic character of this kind of substance that produces the increase in viscosity near to gas-liquid interface.

The analysis of temperature during absorption experiments confirmed the previous conclusions achieved using NMR spectra. A first increase in temperature was obtained when carbon dioxide chemical absorption was produced by means of carbamate formation (exothermic reaction) but when the carbamate hydrolysis increases its importance, a decrease in temperature was clearly detected because this reaction has an endothermic character.

Acknowledgments

The authors thank the Consellería de Economía e Industria of Galicia regional government (Xunta de Galicia) for funding the research through the research project 10MDS265021PR. Authors also thank F. J. Tamajón and EQEA team from University of Vigo their help in thermographic studies. Diego Gómez-Díaz gratefully acknowledges the Ministerio de Innovación y Ciencia of Spain for the support under a “Ramón y Cajal” position.

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Manuscript received July 23, 2013, and revision received Dec. 17, 2013.