HAL
open science

The Use of IR Spectroscopy to Follow the Absorption of CO 2 in Amine media -Evaluation of the Speciation with Time

Etienne Brugère, Jean-Michel Andanson, Karine Ballerat-Busserolles

To cite this version:

Etienne Brugère, Jean-Michel Andanson, Karine Ballerat-Busserolles. The Use of IR Spectroscopy to Follow the Absorption of CO 2 in Amine media -Evaluation of the Speciation with Time. Ying (Alice) Wu; John J. Carroll; Mingqiang Hao; Weiyao Zhu. Gas Injection into Geological Formations and Related Topics, Scrivener Publishing LLC, pp.41-53, 2020, 9781119592068. 10.1002/9781119593324.ch4 . hal-04111878

HAL Id: hal-04111878

https://hal.science/hal-04111878v1

Submitted on 31 May 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Public Domain

The Use of IR Spectroscopy to Follow the Absorption of CO_2 in Amine media - Evaluation of the Speciation with Time

E. Brugère, J-M. Andanson, K. Ballerat-Busserolles

Institute of Chemistry of Clermont-Ferrand, UMR CNRS 6296, University of Clermont Auvergne, Sigma Clermont, 24 avenue Blaise Pascal, 63177 Aubière, France

Abstract

Carbon Capture and Storage (CCS) is a concrete option for CO_2 mitigation in the atmosphere. One option is the CO_2 capture from post-combustion industrial effluents followed by storage in secured sites. Capture processes can be based on selective absorption/desorption cycles of gas into aqueous solutions of alkanolamines[1]. The cost of CO_2 treatment with classical alkanolamines is a limitation for the intensive use of this technology. The SIMODEX project is dealing with coupling experimental developments, molecular simulation and thermodynamic modeling to understand structure-properties relationships, and to develop transferable conclusions to optimize processes at low costs.

This chapter will focus on the use of ATR-IR (Attenuated Total Reflection-infrared) spectroscopy to quantify the speciation in mixtures containing alkanolamine and CO_2, in absence of water, in order to validate the thermodynamic models already used, and to give crucial information for molecular simulation developments.

Introduction

Carbon Capture and Storage (CCS) is a solid option for CO_2 mitigation in the atmosphere. One option is the CO_2 capture from post-combustion industrial effluents followed by utilization or storage in secured sites. Capture processes are generally based on selective absorption/desorption cycles of gas into aqueous solutions of alkanolamines[1]. The following scheme shows the principle of the process.

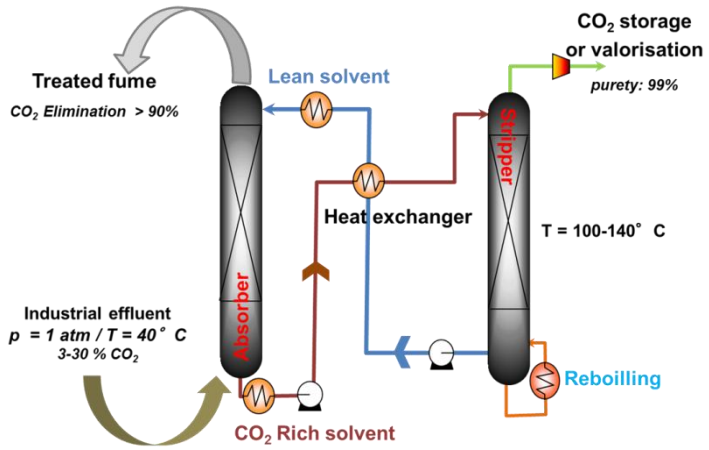

Fig 1: Schematic view of the amine based post-combustion CO_2 capture process.

In this treatment scheme, the industrial effluent is entering in the absorber at atmospheric pressure and at temperature close to 40°C. Due to favorable chemical reactions, and physical absorption, the CO_2 is selectively captured into the aqueous solution, while the other gases are rejected to the atmosphere. The CO_2 rich solvent is then transport to the stripper, where the loaded solution is heated up to 120°C using a countercurrent steam. The CO_2 is then desorbed from the solvent, separated, compressed and transported for further use, while the lean solvent is returned to the absorber. This last step is the most critical in the process cost, as it necessitates high energy consumption for heating up the system. The cost of CO_2 treatment using classical alkanolamine solutions as absorbent is prohibitive and is a clear limitation for the intensive use of this technology.

In order to provide optimized treatment processes, it is necessary to have a comprehensive understanding of the chemical and physical interactions taking place in the mixture. SIMODEX project is a joint program between ANR (Agence Nationale de la Recherche) in France and NSERC (Natural Sciences and Engineering Research Council of Canada) in Canada dealing with coupling experimental developments, molecular simulation and modeling to understand structure-properties relationships, and to develop transferable conclusions to optimize processes at low costs. The objectives of the project are to understand the complex equilibria taking place in the ternary water-alkanolamine-CO_2 system by studying the elementary mixtures starting with pure compounds and going through binary ones as shown in figure 2.

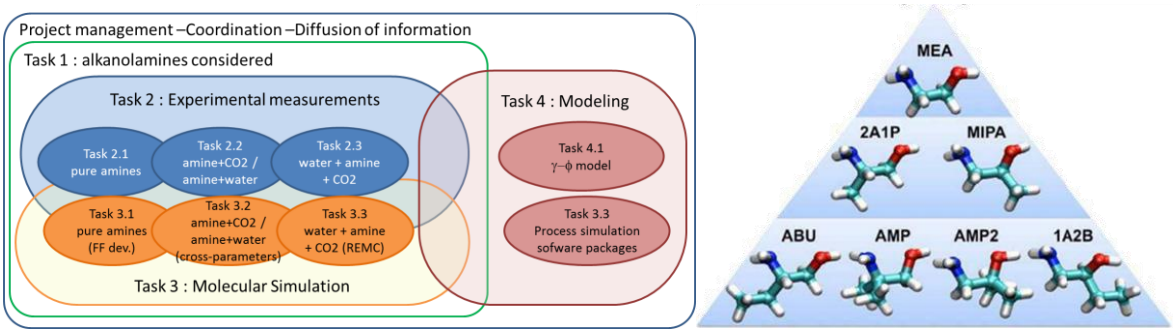

Figure 2: structuration of the SIMODEX project and amine family to be studied

This chapter will focus on the use of IR spectroscopy to quantify the speciation in solutions, in order to validate the thermodynamic models already used, and to give crucial information for molecular simulation developments. The mixtures chosen are binary systems containing initially only amine and CO_2, where there is almost no publication in the literature. For this binary mixture the only reaction that may happen during the mixing process is the formation of the carbamate that can be written as following:

$$2 \cdot HOCH_2CH_2CH_2NH_2 + CO_2 \rightarrow HOCH_2CH_2CH_2NHCOO^- + HOCH_2CH_2CH_2NH_3^+ \qquad \text{eq.1}$$

As experimental issues happened when studying CO_2-monoethanolamine (MEA) mixtures, such as high increase in viscosity or solid phase formation, a physical solvent, known for not interacting with amine or CO_2 was used. Then ethylene glycol was chosen to dilute the system. [2]

More specifically, the speciation in mixtures containing MEA + ethylene glycol + CO_2 will be studied using IR-spectroscopy, and a new *in situ* cell designed for following absorption of gas in liquid mixtures versus time will be described and first promising results are presented.

Materials and Methods

Chemicals

Monoethanolamine (MEA) was purchased in TCI-europe (purity >99%), ethylene glycol is from Riedel and Haën (purity 99.5%) and CO_2 from air products (99.995%). The water quantities in liquids were verified using Karl Fisher measurements, and correspond to 300 ppm and 1000 ppm respectively for amine and glycol.

Sample preparation

As direct measurements of MEA+CO_2 mixtures were not possible due to increase of viscosity and solid phase generation, the MEA was first mixed with a CO_2 physical solvent, namely the ethylene glycol. A first concentration of 30% of MEA in ethylene glycol was chosen as this is comparable to the classical concentration of MEA in water when studying the solvents used in the process. Then a second concentration of 10% MEA in ethylene glycol was considered to reach more easily the complete stoichiometric reaction of the CO_2 on MEA.

Experimental device

The spectroscopic measurements, realized at atmospheric pressure and room temperature, were performed using a heatable Golden Gate™ accessory (Specac, Ltd., UK) with a diamond as ATR (Attenuated Total Reflection) crystal. The ATR-IR spectra were collected by means of Thermo Nicolet™ 380 FT-IR spectrometer with a DTGS (deuterated triglycine sulfate) detector. The spectra were obtained with a resolution of 4 cm^{-1}, 32 co-added scans and were recorded in the range of 4000 – 500 cm^{-1}. The measurement of one spectrum takes around 50 seconds.

For the spectroscopic measurements under pressurized CO_2 a heatable Golden Gate™ accessory (Specac, Ltd., UK) equipped with a home-designed pressurized cell was used. Briefly, the Golden Gate™ was used to hold the ATR crystal with an incident angle of 45◦ below the liquid phase of interest. Some modifications on the design of the bridge were realized to support a customized sapphire cell as shown in figure 3. Two aluminum arms (1) were added to the bridge to increase the space between the thumb screw and the diamond in order to fit with the new high volume cell (2+4) and a stirring mechanism (3).

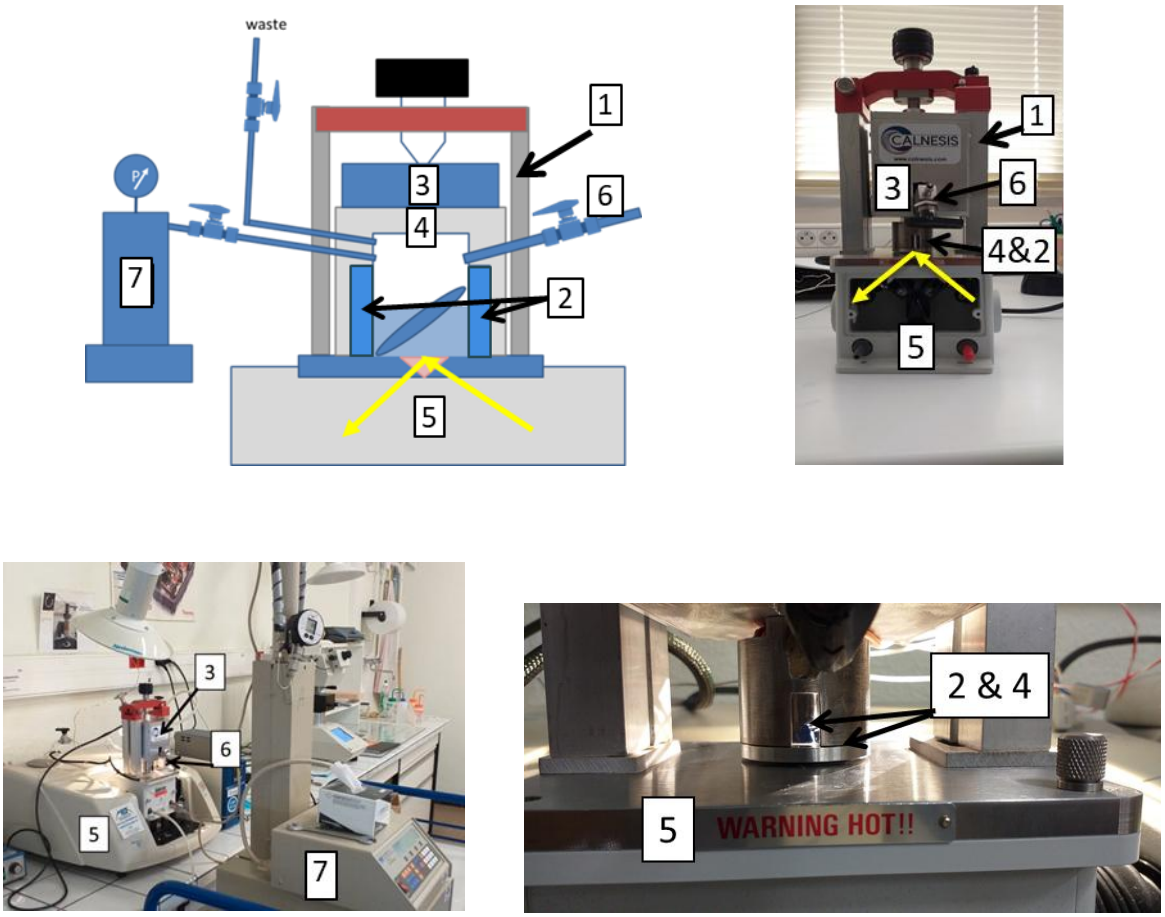

Figure 3 : New experimental setup for gas absorption : 1. Aluminum arms; 2. sapphire cylinder; 3. magnetic stirrer; 4. inox cell, surrounding sapphire cylinder; 5. ATR-IR spectrometer; 6. liquid injection valve; 7 high pressure pump equipped with pressure transducer and gas injection valve.

The liquid cell was installed on the top of the heating plate of the Golden Gate™ as shown on figure 3. The internal volume of the cell is about 2 ml. The cell is composed of a sapphire cylinder surrounded by an inox block. Heating cartridges and PT100 resistances are inserted in the inox cylinder to control the temperature of the sample. Two windows are present in the inox cylinder, so the inside of the cell can be observed during the whole experiment. A Teflon ring was installed between the cell and the plate to prevent leaking.

The liquid is inserted using the injection valve (6) until the needed volume of liquid is obtained. About 1 mL of liquid is introduced in the cell. After reaching the temperature equilibrium, the gas is added using the gas injection valve, while the pressure is maintained constant using the high pressure syringe pump. As the magnetic stirrer is agitating the solution, the diffusion of the gas in the liquid starting immediately.

The IR spectra are then recorded every minute from the beginning of the experiment. When the evolution of the peaks is reduced, the spectra are measured every 5 minutes, until the signal becomes constant, or when the gas contained in the high pressure pump is consumed.

Results and discussion

Kinetic of absorption

A first kinetic experiment was realized using a liquid mixture containing initially MEA (10% w/w) and ethylene glycol (90% w/w). IR spectra of direct measurements are reported on the top figure 4. The mixture was introduced in the cell, and a first spectrum was realized. Then the valve isolating the CO_2 from the system was open and the gas started flowing in the head space of the cell.

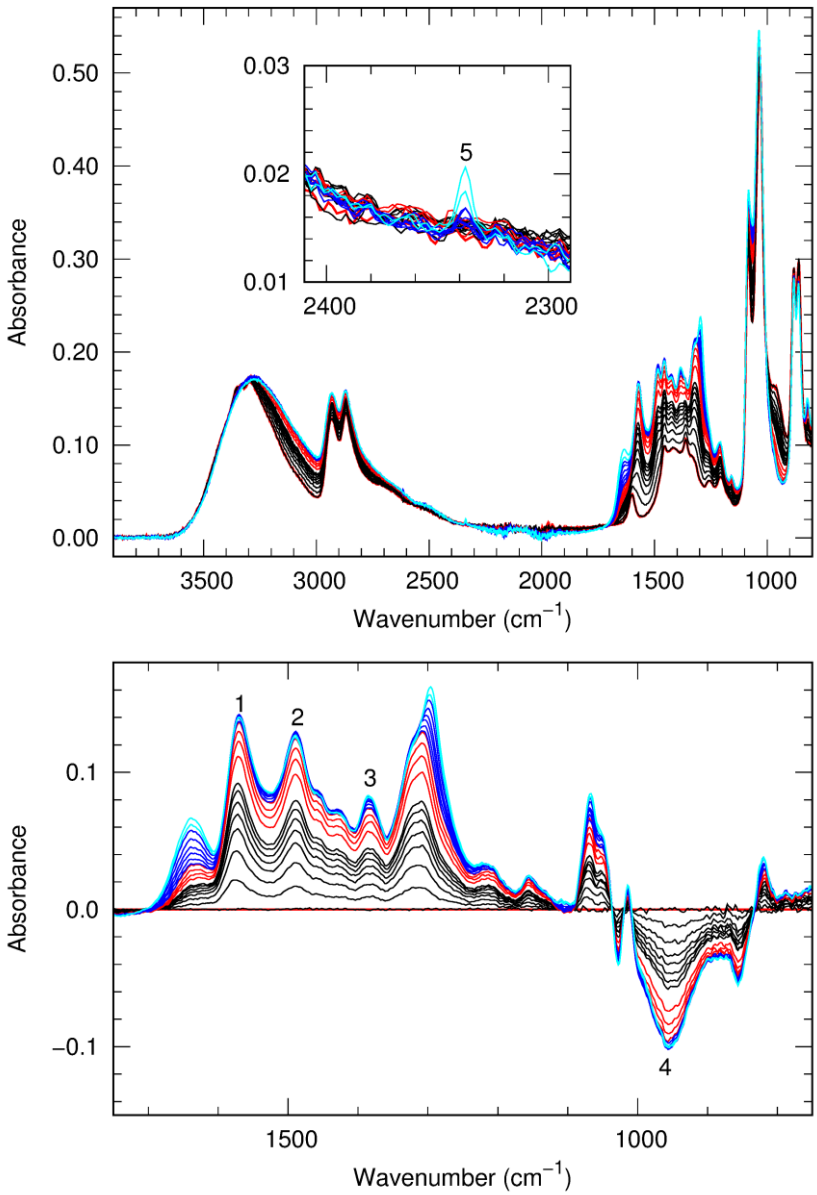

Figure 4 : IR spectra during the kinetic of the sorption of CO_2 in MEA-Ethylene glycol mixture (top) and MEA-Glycol-CO_2 after subtraction of the MEA-Glycol spectrum (bottom) at different time; 1-3 peaks : characteristic peaks for carbamates ; 4 : characteristic peak for non-protonated amine; 5 : asymmetric stretching vibration band for physically absorbed CO_2. The spectra obtained during the first 10 minutes are the black ones. The red spectra are obtained for time from 10 to 40 minutes, while blue ones are for times higher than 40 minutes after the beginning of the CO_2 sorption.

In order to interpret the results, the spectrum obtained for the binary mixture without gas (t=0 minute) was subtracted to the subsequent spectra as shown on the bottom figure 4. All positive peaks after subtraction are characteristics of new species appearing in the liquid during the sorption while negative peaks correspond to the disappearance of pre-existing species. In order to quantify the speciation versus time in such systems, it is necessary to determine a relation between the intensity of the IR signals and the quantity of each species.

Calibration of speciation

Sample preparation

In order to realize the calibration of the absorption of CO_2 in MEA as function of the loading charge, it was necessary to record spectra containing very well know concentrations of MEA and CO_2. For that purpose, a mixture of MEA + ethylene glycol was prepared by weight. Then CO_2 was added above the liquid sample, for 12 hours, under a pressure of CO_2 of 0.2 MPa (2 bar), while the liquid phase was agitated using a magnetic stirrer. Then the mixture was returned to atmospheric pressure. The sample was then weighted, and the mass difference with the sample without CO_2 was considered as corresponding to the mass of CO_2 absorbed in the sample. This very concentrated sample was diluted using the initial mixture of MEA+Glycol, in different proportions to reach various CO_2 loading charges.

Spectra and results

The spectra obtained for the calibration are given in figure 5. The first graph shows the direct spectra obtained for mixtures at known loading charge, from α=0 to 0.5 (α = mol of CO_2 / mol of amine)while the second one present a zoom of the fingerprint region (1700 – 750 cm^{-1}), where most of the bands of organic compounds are regrouped. The red spectrum corresponds to the sample obtained for MEA+Glycol solution without CO_2.

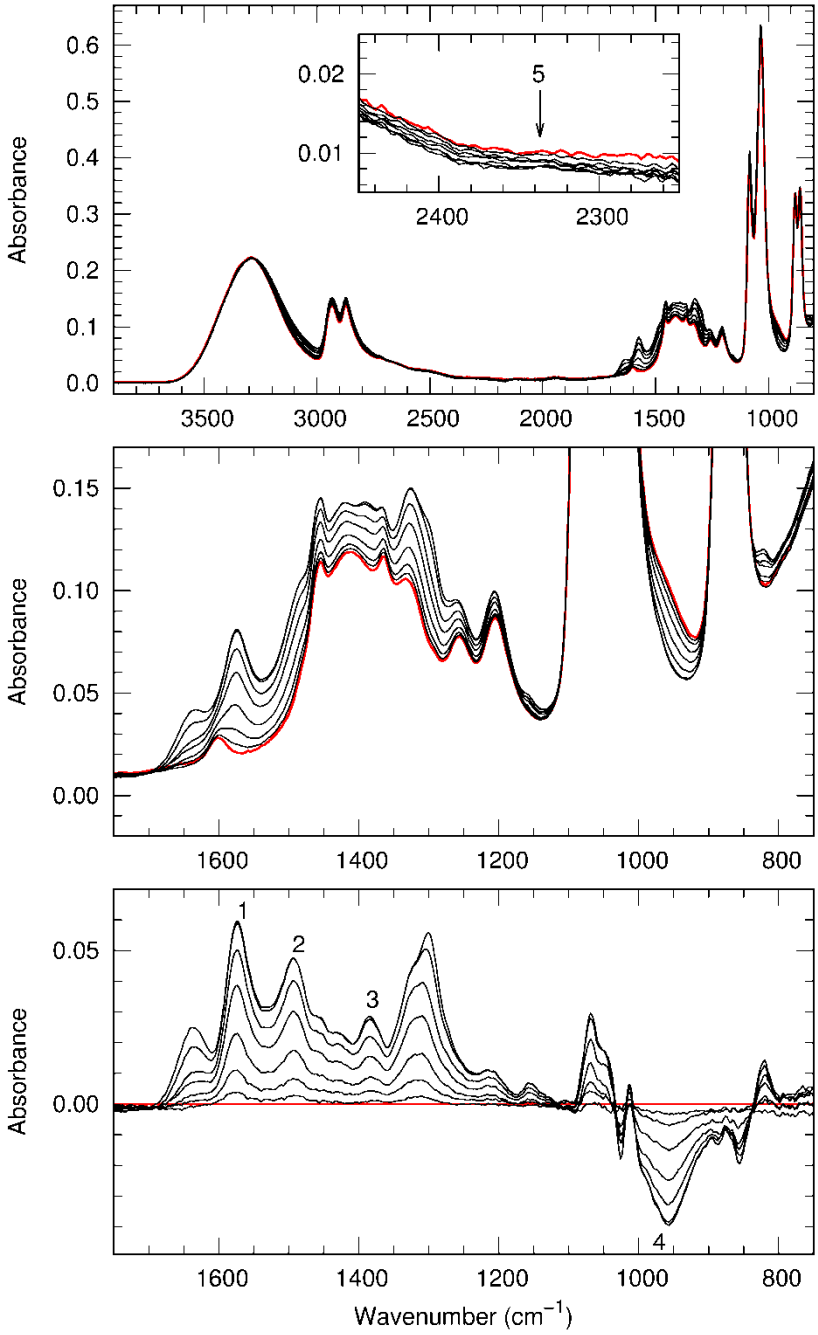

Figure 5: IR spectra for mixtures containing MEA (30%) ethylene glycol (70%), at different and well known loading charges from a = 0 up to a = 0.53. top figure: direct spectra; middle figure: zoom of the spectra in the range of 1700-750 cm^{-1}; bottom figure: fingerprint region of the IR spectra of the MEA-ethylene glycol-CO_2 mixtures after subtraction of the MEA-ethylene glycol spectrum.

As previously described, and in order to be able to analyze the results, the red spectrum was subtracted to the others as shown on the third graphic of figure 5. On this graph, 4 peaks have been identified and used to calibrate the amount of absorbed CO_2. Peaks labelled from 1 to 3 correspond to peaks characteristic of vibration in carbamate molecules [3]. The peak 4 centered at 960 cm^{-1} is characteristic of non-protonated nitrogen of MEA [3]. When increasing CO_2 loading charge, the height of all those peaks increases. Peaks 1 to 3 are more and more positive while the peak 4 is more and more negative. This corresponds naturally to the generation of carbamate and consumption of non-protonated MEA following

the equation 1 shown above. The signal corresponding the physisorbed CO_2 (band label 5 in figure 5 at around 2340 cm^{-1}) has not been detected for the concentrations realized during the calibration.

In order to calibrate the system, it is necessary to relate the height (or the area) of each peak to the loading charge. The peak 4 was truncated on the left side due to peak displacements during the absorption. Then, for this peak we considered the height of the peak as the characteristic data. For peaks 1 to 3 it was possible to use the integration that reduces the uncertainty on the result. The curves representing area of peaks 1 to 3, and height of peak 4 versus loading charge are given in figure 7.

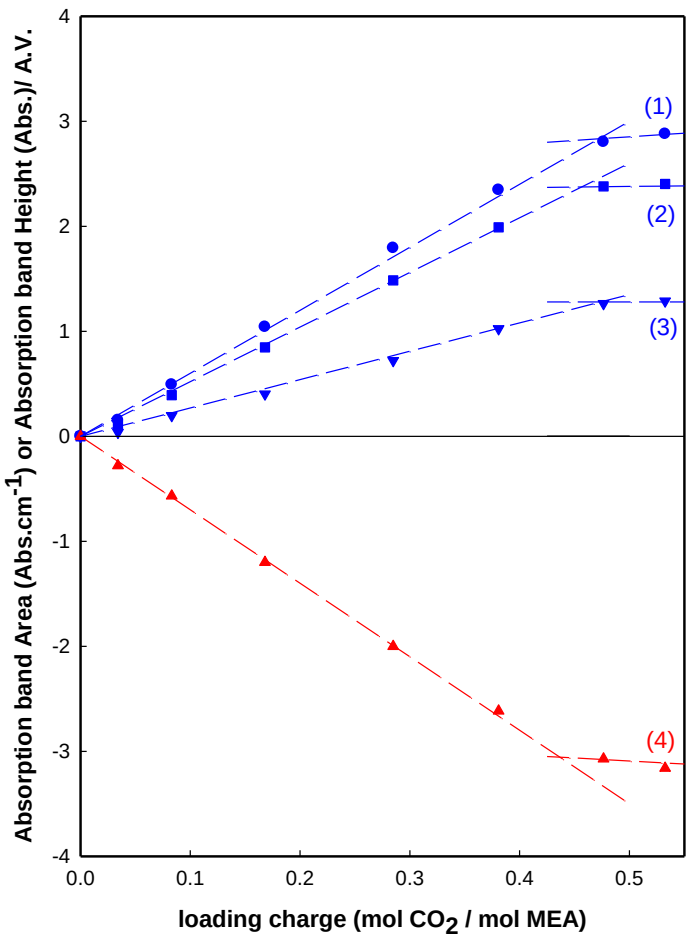

Figure 6 : area (peak 1 to 3) and height (peak 4) of the IR signals characteristic to chemical reaction occurring in the mixture.

From those calibrations, it is then possible to recalculate at any time of a kinetic experiment the quantity of each species formed when the loading charge is below 0.45. When the concentration of CO_2 is higher the increase of the IR signals are much slower, probably part of the CO_2 does not react but is physisorbed. Furthermore, it was not possible to prepare mixtures containing high amount of CO_2 physically absorbed in the binary mixture. For that purpose, CO_2 was then absorbed in pure ethylene glycol under higher pressure directly in the ATR-IR cell.

Physisorption

As it can be seen on figure 4, during the kinetic of the CO_2 sorption in the MEA-Ethylene glycol mixture, after one hour, it is possible to observe a small signal at around 2340 cm^{-1} corresponding to the

asymmetric stretching vibration of the CO_2 physically absorbed in the mixture. In order to quantify this CO_2, it is then necessary to calibrate this band. For that purpose, a mixture of ethylene glycol + CO_2 was measured at high pressure.

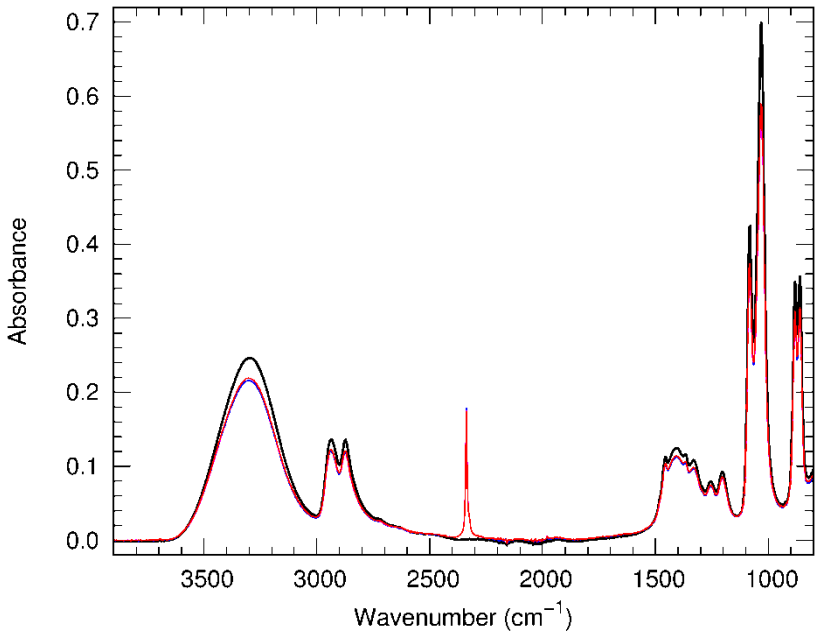

Figure 7: IR spectra for pure ethylene glycol (black curve) and CO_2 in ethylene glycol (red and blue curve) at 20.0 bar and 35°C.

On figure 7, the black curve show the signal obtained for pure ethylene glycol. Measurements have then been realized for mixtures of CO_2 + glycol, at 2.0 MPa, 35°C at different times. Two spectra obtained for different times are shown on figure 7 (red and blue spectra). Two phenomena have to be observed. The intensity of all bands corresponding to the ethylene glycol is decreasing with the sorption of CO_2. These decreases of intensity are explained by the swelling of the solvent due to the presence of CO_2. This phenomenon is well known and documented in the literature, particularly in the case of liquid [4,5].

When looking at absorbance close to 2340 cm^{-1} it is easy to observe an intense peak corresponding to the CO_2 physically absorbed in ethylene glycol. The rest of the spectra is identical with and without CO_2, apart from the decreasing of the intensity of bands corresponding to the swelling of the ethylene glycol, meaning that no chemical reaction happened in those mixtures. The area of the CO_2 peak at 2340 cm^{-1} can then be directly associated to the solubility of CO_2 in ethylene glycol using literature value [6], at this temperature and pressure, the solubility of CO_2 in ethylene glycol is x_{CO2} = 0.0369±0.0006. Admitting that the absorption of CO_2 in ethylene glycol follow the Beer-Lambert law, a linear regression was determined between zero and this concentration to estimate the quantity of CO_2 absorbed in solutions of interest.

<u>Full curve speciation</u>

The evolution of absorptions of the characteristic bands of different species versus time shown in figure 5, were plotted in figure 8. Carbamate vibrations are shown in blue, while the vibration of the none-protonated amine group of MEA is in red. The signals of the physically absorbed CO_2 in the MEA-Glycol mixture correspond to the black empty circle.

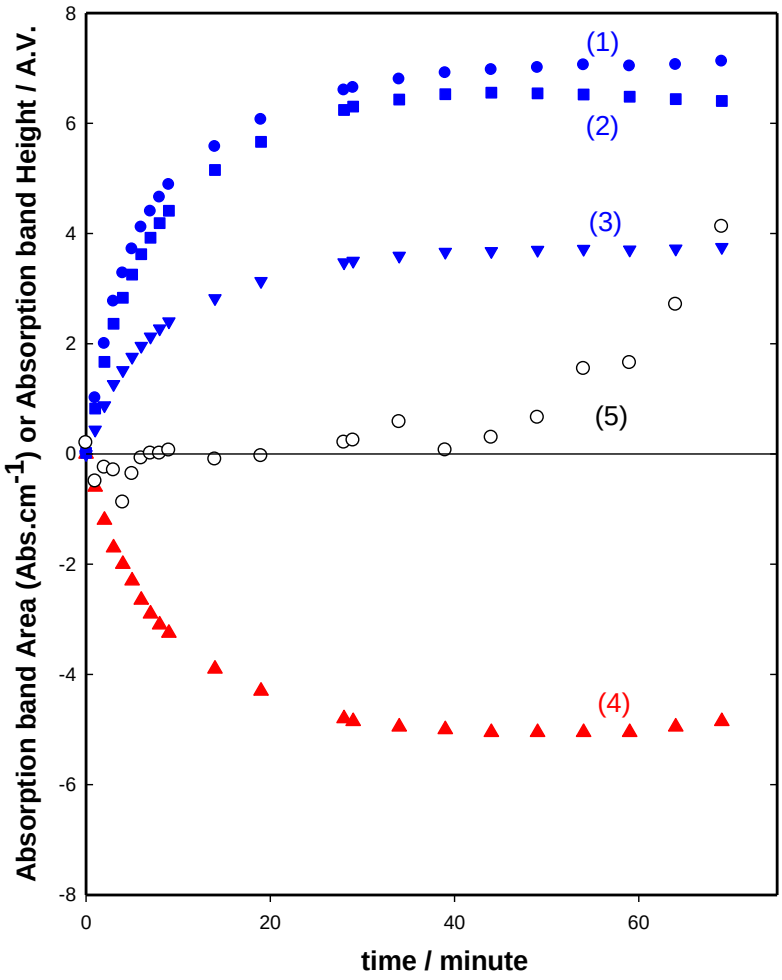

Figure 8: Area/height of the peaks versus time. Blue curves: area of characteristic peaks for carbamate (wavelength 1573, 1495 and 1385 cm^{-1} respectively for peaks 1 to 3); red curve: height of characteristic peak for non-protonated MEA (peak 4); black circle: area of characteristic peak for physically absorbed CO_2 (peak 5; signal multiply by 100 for visibility).

On this figure one can see that the absorbance area for peaks corresponding to carbamate increases quickly during the 20 first minutes. The quantity of none protonated amine decreases synchronously to the appearance of carbamate. All the blue and the red curves reach a plateau after 30 minutes. Using the calibration curves shown before, at this time, the value of absorbance correspond to a loading charge of about 0.4. Parallel, during the first 40 minutes, no peak for physical absorption is observed. After this time, the intensity of the band starts to increase continuously. After 70 minutes the CO2 physically absorbed corresponds to a molar fraction of 0.002. With this graph, it is confirmed that the chemical reaction is the first step of the process, while the physical absorption starts only when most the non-protonated amine has react with CO_2 to form carbamate and protonated amine.

Conclusion

In situ ATR-IR spectroscopy has been used successfully to follow the absorption of CO_2 in binary liquids containing MEA and ethylene glycol. The spectra obtained have shown peaks characteristic of carbamate formation, and none protonated amine consumption. After calibrating the signal, the area

of the peaks linked to carbamates, and the height of the peak corresponding the none protonated amine has been associated to an advancement of the reaction of formation of carbamate.

The same experiments will be carried out with amines with a skeleton similar to MEA, as shown on figure 2. The results obtained will allow evaluating the influence of the substituents on the carbons of the MEA on the chemical reaction leading to carbamate formation. It will be possible to compare the kinetic of the reaction as well as the final advancement of the reaction.

Aknowledgements

This work is part of the international project SIMODEX supported by ANR in France and NSERC in Canada. The authors also acknowledges the financial support received from the Agence Nationale de la Recherche of the French government through the program ''Investissements d'Avenir'' (16-IDEX-0001 CAP 20-25).

references

[1] L. Raynal, P-A. Bouillon, A. Gomez, P. Broutin*, Chemical Engineering Journal* 171 , 742, 2011
[2] C-H. Yu, C-H. Huang, C-S. Tan, *Aerosol and Air Quality Research,* 12: 745–769, 2012
[3] C. Sun, P. K. DuttaInd. *Eng. Chem. Res*, 55 :22, 6276-6283, 2016 [4] I. Pasquali, J-M. Andanson, S. G. Kazarian, R. Bettini,The Journal of Supercritical Fluids, 45:3, 384-390, 2008
[5] J-M. Andanson, F. Jutz, A. Baiker. J. Phys. Chem. B, 113 :30, 10249-10254, 2009,
[6] X. Gui, Z.G. Tang, W. Fei, *J. Chem. Eng. Data*, 56, 2420–2429, 2011,