

Measuring water in CO₂ mixtures relevant to Carbon Capture and Storage (CCS)

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ABSTRACT

Carbon Capture and Storage (CCS) is one of the more important current strategies to reduce CO₂ emission into the atmosphere. The motivation for the work described here is to provide fundamental studies to ensure the safety of anthropogenic CO₂ transport via pipeline in the CCS process by determining the water quantity limits in CO₂ mixtures. Our investigations show for the first time that the solubility of water in CO₂ containing small percentages of impurities at 40°C in the pressure range 8.89 to 17.24 MPa is dramatically different to those in pure CO₂. We have utilised two separate methods to perform these measurements. Initial results have been obtained in-situ using a high pressure-high temperature set-up coupled to an FT-IR spectrometer. Our second approach uses Karl Fischer titration both to corroborate our results obtained using FTIR and also to allow further investigations particularly at lower temperature conditions. Here we describe in detail the FTIR approach for such measurements.

INTRODUCTION

Over recent years, the growth in human activity has involved a sharp increase in CO₂ emissions. The repercussions for the environment are significant since CO₂ is one of the main gases responsible for the greenhouse effect.[1] Thus, reducing the CO₂ release rate is urgent and currently one of the priorities of the scientific community. In this context, there is major activity in the area of Carbon Capture and Storage (CCS).[2; 3] This process consists of trapping CO₂ directly from the emission source and storing it underground in depleted gas/oil or coal reservoirs. Some pilot plants are already operating in the USA and in Europe, for example, located next to power plants; these show encouraging results, reducing emissions by 16% in 2011.[4] Many of the reported studies on CCS have focused on CO₂ capture.[5-9] Nevertheless, much work remains to be undertaken particularly in the area of transportation to make CCS safe and sustainable in the long-term. In particular, a high water content in the captured CO₂ can lead to corrosion of the pipes.[10-13] There are a variety of different capture methodologies (post-combustion, oxy-fuel or pre-combustion) that will be employed and it is expected that in all cases the captured CO₂ could contain a small percentage of impurities including water and other gases such as N₂, H₂ or Ar. [14-17] The presence of liquid water can have lead to major enhancement of corrosion which could eventually cause the rupture of the pipelines with dramatic consequences. To prevent water precipitation out of the CO₂ stream during transport, it is necessary to understand how these impurities can affect the phase behaviour of the CO₂ and possibly the solubility of the water. In the literature, there are reports on the solubility of water in pure CO₂[18-30] By contrast, very few studies have been reported on ternary systems H₂O + CO₂ + impurities [31-33] and none of them elucidate the solubility of water in anthropogenic CO₂. However, these impurities can significantly change the thermodynamic properties of CO₂. Recent work in our group has focused on the

density of CO₂/N₂ and CO₂/H₂ mixtures and highlighted how a low percentage of N₂ or H₂ can induce significant changes in the density near the critical point [34]. This consideration prompts us to investigate the solubility of water in the dense phase CO₂ in order to simulate conditions in captured CO₂ streams, and to study the effect of impurities on the solubility of H₂O in CO₂. All the measurements have been carried out *in-situ* using an original high pressure-high temperature set-up coupled to an FT-IR spectrometer. There have been a few publications on measuring water solubility in pure CO₂ using FT-IR spectroscopy [28; 35]. FT-IR is a widely used technique which has already shown its great efficiency for the study of compounds in supercritical fluids [36-38]. More specifically, we have focused our study on the mid-IR region which has allowed us to work with very small amounts of gas and water since water has a strong absorbance band located at 1600 cm⁻¹. In addition, we have a second complementary approach to validate our FT-IR measurements by an independent technique to ensure the accuracy of our findings. This independent method involves coupling a high-pressure set-up with a Karl Fischer titrator. Karl Fisher titration is an electrochemical reaction which has shown a good efficiency in detecting trace of water in gaseous samples. Furthermore, the set-up has been developed to work efficiently at lower temperatures in order to reach CCS conditions more easily. This paper focuses on our FT-IR method.

MATERIALS AND METHOD

Infrared set-up

Figure 1 gives a schematic representation of the device used in this work. FTIR spectroscopic measurements have been performed using a Nicolet 380 spectrometer equipped with an DTGS detector and a Ge/KBr beam splitters with a spectral range between 350 -7800 cm⁻¹. The spectrometer was purged with dry air. Single beam spectra were recorded with a 4 cm⁻¹ resolution and were obtained after the Fourier transformation of 32 accumulated interferograms.

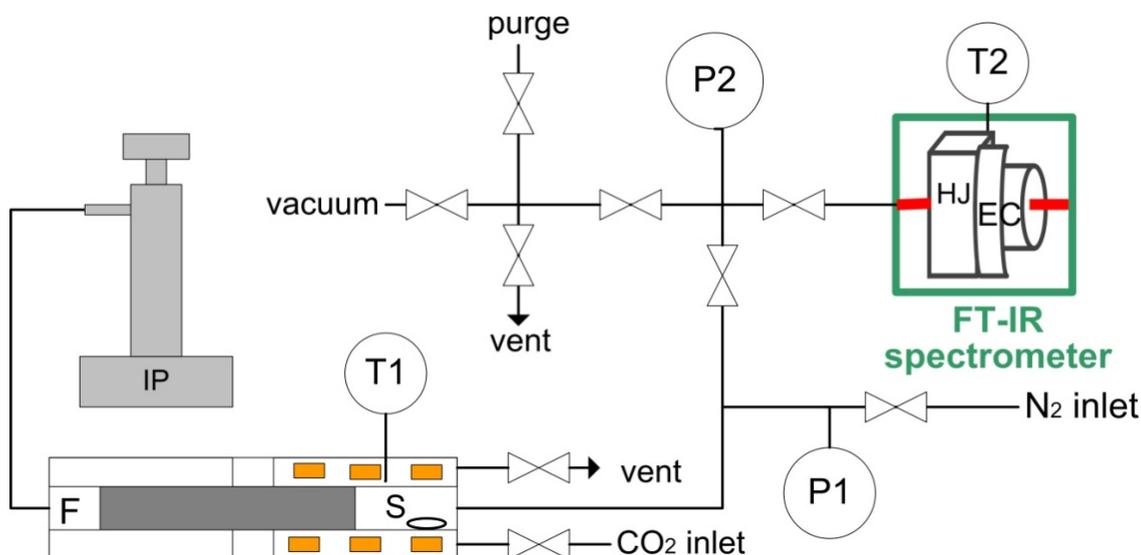


Figure 1: High pressure – high temperature controlled set-up combined with an FT-IR spectrometer: the components are labeled as follow: IP - syringe pump; F – transmitting fluid; S-Sampling Chamber; T1- temperature controller for the gas mixer; P1-pressure transducer (0-2MPa); T2- temperature controller for the FT-IR cell; P2-pressure transducer (0-34 MPa); HJ-heating jacket; EC- infrared equilibrium cell

The infrared optical cell developed in Nottingham is equipped with two cylindrical CaF₂ windows separated by a pathlength of 3 mm. Windows are sealed to the body of the cell and window holder using an epoxy resin mixture then the window holder was sealed to the body *via* a Teflon O-ring. A heating jacket fits around the cell controlling the temperature inside to within ± 0.3 °C by means of a K-type feedback thermocouple. A more detailed description of this cell has already been published [39].

Volume variable gas mixer

The mixtures CO₂/N₂ were prepared using a stainless-steel sample mixer which has been described in detail previously [34]. This cylindrical unit consists of a variable-volume sample chamber separated by a piston from another chamber filled with isopropyl alcohol (IPA). The system is connected to a syringe pump (ISCO) which allows pumping or withdrawing of IPA in order to move the piston forwards or backwards and so regulate the volume of the sample chamber. The mixer has a custom built mixing mechanism and a heating jacket monitored by a thermocouple (K-type) mounted in the chamber wall. The pressure inside the sample mixer is monitored by two pressure transducers (RDP SuperTJE) with maximum pressure ratings of 2 MPa and 34.5 MPa, respectively, and a stated accuracy of $\pm 0.05\%$ of full scale.

Experimental method and uncertainty

Firstly, a mixture CO₂/N₂ was prepared in the gas mixer at room temperature. The nitrogen was first injected at a pressure controlled by the output of P1 pressure transducer. Using the NIST database we were able to determine the density of N₂ and so to determine the amount of CO₂ needed to complete the mixture. Then the mixture was heated at the desired temperature and left stirred 2 hours to ensure the homogeneity. Secondly, the gas mixture was injected in the optical cell heated at the right temperature and containing a know amount of water. Then the mixture water + CO₂ + N₂ was stirred 2 minutes before collecting the infrared spectra. During the stabilization of the operating conditions, consecutive spectra were recorded every 5 minutes. The equilibrium was considered to be achieved when no further changes of the spectral bands was observed in several consecutive FTIR spectra. The equilibrium was normally reached in less than 10 minutes. For each system, several experiments to determine the saturation points were carried out to ensure a good reproducibility in our measurements at specified conditions of temperature and pressure. For our initial points, the final saturation value was the average of 15 separate measurements.

RESULTS

Figure 2 shows a typical IR spectrum in the region of interest for this work. The band assigned to the ν_2 bending mode of water at 1600 cm^{-1} was clearly visible although the IR absorbance is lower than the value corresponding to the saturated concentration of H₂O under these conditions. Our investigations have focused on using this band to determine the saturation of H₂O in mixtures of relevance to CCS.

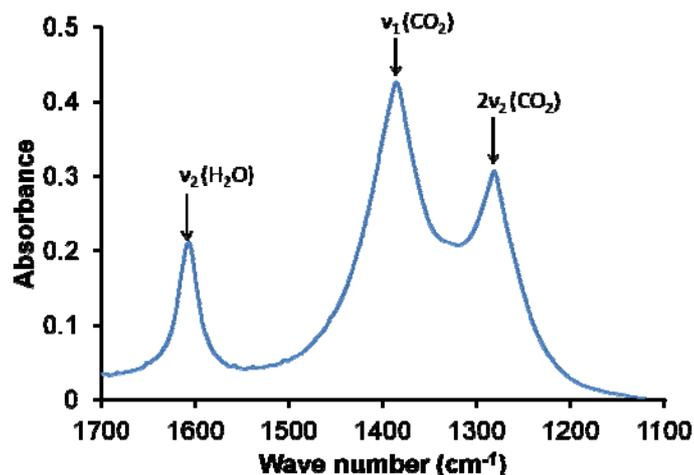


Figure 2: FT-IR spectrum of H₂O in CO₂ at 25°C, 9 MPa and with 0.2 μl of H₂O: the bending mode of water has been used to determine the amount of water in the CO₂ + N₂ mixture, since the band was not obscured by the Fermi band of CO₂

For each value of temperature and pressure, increasing volumes of water were added to the CO₂ + N₂ mixture. Figure 3 a) displays the increase in absorbance of the water bending mode as a function of the amount of water added. These spectra have been obtained after spectral subtraction of the CO₂ bands. We can clearly see that the H₂O band increases with the volume of water from 0.1 to 0.6 μl until we reach a threshold. Indeed, the absorbance of the H₂O band remains constant, which means that no more water can be dissolved in the CO₂ phase. In these conditions, we considered that the CO₂ phase was saturated with water.

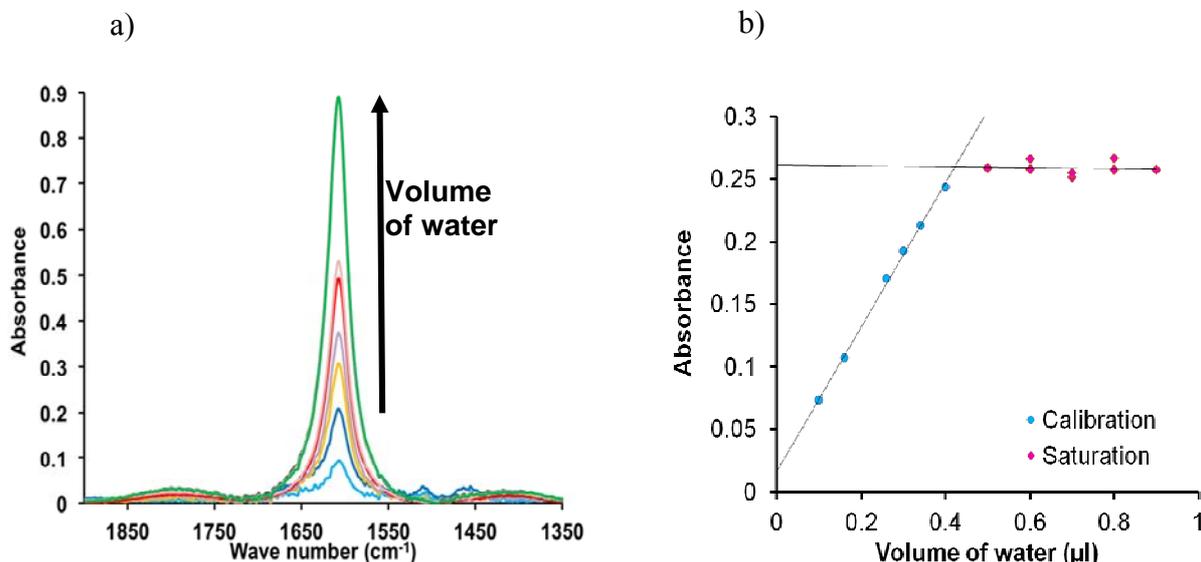


Figure 3: a) Evolution of IR band of H₂O bending mode at 1600 cm⁻¹ as a function of the volume of H₂O at 40°C and 12.5 MPa, with corrections for the CO₂ spectra.
b) Evolution of the absorbance of the infrared H₂O band at 1600 cm⁻¹ as a function of the volume of the water introduced in CO₂ + N₂ mixture at 25°C and 12.5 MPa.

In order to determine the saturation volume of water accurately, the absorbance of the H₂O ν₂ band has been plotted as a function of the volume of the water. Figure 3(b), shows the typical

diagram which we obtained at a given temperature and pressure. Two linear trend lines fit both the calibration and the saturation data and the intersection of the two lines is defined as the saturation quantity.

Firstly, we have validated this method by reproducing data available in the literature on the solubility of water in pure CO₂. Figure 4 displays the results obtained in this work at 40°C in the pressure range between 8 and 14 MPa.

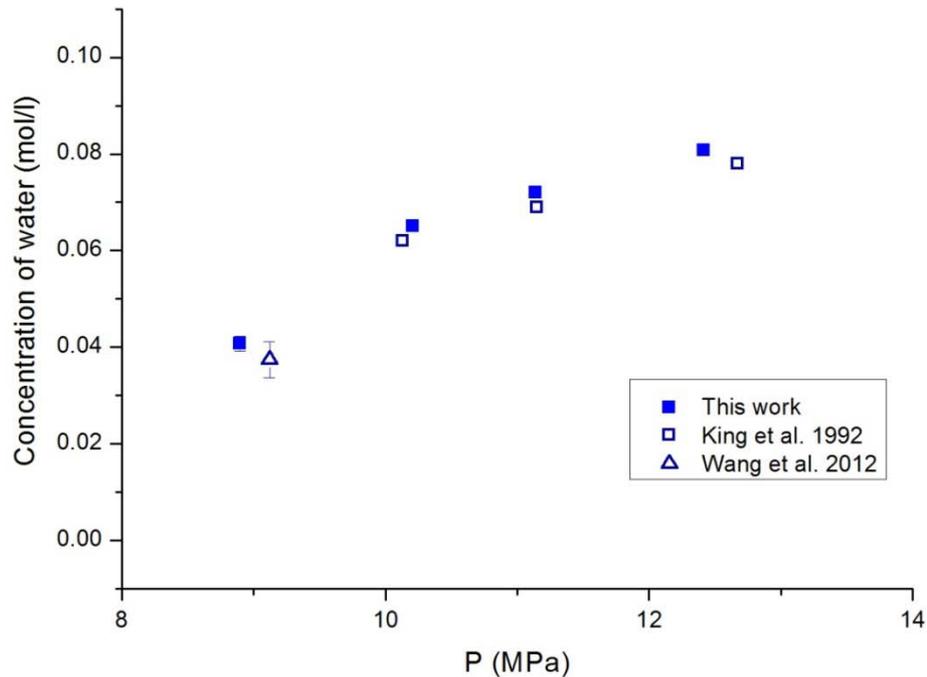


Figure 4. Evolution of the molar concentration of water in: pure CO₂ 40°C as a function of the pressure. Comparison between this work and other publications in the conditions of interest (King et al.[27] and Wang et al.[40])

Our measurements, reported in Figure 4, present an uncertainty of less than 4% whereas in the literature values by Wang et al.[42] have an uncertainty of 10 % using a similar method. Nevertheless, our results are in very good agreement with King *et. al.*[29]

Finally, all our work has then focused on the solubility of water in CO₂ + CCS mixtures using the same methodology. Highly reproducible measurements were obtained at 40°C over the pressure range 8.89 to 17.24 MPa.

CONCLUSION

An efficient and reliable FT-IR method has been developed to determine the solubility of water in CO₂ + CCS impurities. Our study shows that the presence of impurities changes significantly the mole fraction of water in CO₂. The evolution of the mole fraction of water as a function of the pressure shows an influence of the density in the solubility of water in both CO₂ and CO₂ + CCS mixtures. We have seen that whatever the mixture, at 40°C the mole fraction of water decreases at lower pressure until a minimum after which it starts to increase again. This minimum is shifted with the presence of impurities. Thus, these results show that the presence of impurities affects the solubility of water in CO₂ and represent important data for the safe CO₂ transport in view of Carbon Capture and Storage.

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