Experimental mutual solubilities of CO\textsubscript{2} and H\textsubscript{2}O in pure water and NaCl solutions.

Marie-Camille Caumon\textsuperscript{1} Jérôme Sterpenich\textsuperscript{1} Aurélien Randi\textsuperscript{1} Jacques Pironon\textsuperscript{1}

\textsuperscript{1}Université de Lorraine, CNRS, CREGU, GeoRessources laboratory, BP 70239, F-54506 Vandéœuvre-lès-Nancy, France

The solubility control in the H\textsubscript{2}O-CO\textsubscript{2} system under high pressure is a key parameter of CO\textsubscript{2} geological storage. Numerous studies were published under various pressure-temperature-composition (PTX) ranges to cover CO\textsubscript{2} storage conditions, in particular in the H\textsubscript{2}O-CO\textsubscript{2} system. If CO\textsubscript{2} solubility in pure water is rather well documented at temperature higher than 100 °C, measurements in conditions relevant to CO\textsubscript{2} storage are sparse, at T > 31 °C and P > 74 bar with the addition of salt. There is also a lack of experimental solubility data of water in the CO\textsubscript{2}-rich phase (Marini, 2006; Spycher et al., 2003). These experimental data are crucial to constraint most of the thermodynamic models (e.g. Duan et al., 2006; Dubessy et al., 2005; Spycher et al., 2003; Truche et al., in press).

In this study, the experimental solubility data of CO\textsubscript{2} in the H\textsubscript{2}O-rich and of H\textsubscript{2}O in the CO\textsubscript{2}-rich phases are both acquired. An experimental device (IMAGES, Sterpenich et al., 2009) was built to measure mutual solubilities in the CO\textsubscript{2}-H\textsubscript{2}O system without sampling, using Raman immersion probes (Figure 1).

![Figure 1: the IMAGES experimental device.](image-url)
The device consists of a 316 stainless steel autoclave of a volume of 2 L placed in a band heater and connected to a hydropneumatic pump to inject CO₂. A Teflon bowl is placed in the autoclave to avoid the contact of the aqueous solution with steel and so, to reduce the risk of chemical contamination through corrosion and to remove laser reflections on the metallic surface of the autoclave. The device runs at a maximum pressure of 300 bar, and a maximum temperature of 250 °C. The temperature of the oven is controlled by a thermocouple put in a stainless steel thermowell and dipped into the autoclave. The top of the autoclave is covered with alumina wool to limit heat convection inside the autoclave by thermal isolation. Pressure and temperature are externally controlled and continuously monitored and recorded. Temperature is calibrated using a field metrology well with 0.35 °C accuracy in the range 50-250 °C, and controlled to ± 0.1 °C. The pressure transducer is calibrated using a Fluke pressure calibrator (range of 0 to 350 bar) with an accuracy of 0.05 % of full scale (i.e. 0.2 bar).

The system was first calibrated by measuring the Raman signal of CO₂ in water and of water in the CO₂-rich phase at 100 °C from 5 bar to 200 bar (Caumon et al., in press). The peak intensity ratios I_{CO2}/I_{H2O} and peak area ratios A_{CO2}/A_{H2O} were correlated to calculated solubilities (Duan and Sun, 2003) with uncertainties of a few percents. In the present study, new data are acquired in an extended range of temperature (up to 150 °C) and with salt (NaCl) in a range where there are few experimental data. The peak area ratios and peak intensity ratios are correlated to calculated solubilities (Duan et al., 2006; Spycher et al., 2003; Truche et al., in press) and compared to literature. The effect of salt concentration and temperature on the calibration curves is discussed.

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