Study of SO$_2$/water and NO/water/salt systems from 25 to 150$^\circ$C using fused silica capillaries, batch autoclave and Raman microspectrometry

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Abstract

Depending on CO$_2$ capture processes or hydrocarbon sources, fuel gas from boilers can be accompanied with impurities which could be co-injected in a geological storage. These gases, such as SOx, NOx, or oxygen could interact with reservoir fluids and rocks and well materials and could affect the safety of the storage. However, there are currently only few data on the behavior of such gas mixtures, as well as on their chemical reactivity, especially in the presence of water. The purpose of this paper is to develop experimental and analytical protocols in order to acquire new thermodynamic data on SO$_2$ and NO under geological conditions of pressure and temperature using Raman spectrometry.

1. Introduction

Regarding the hydrocarbon source and CO$_2$ capture processes, fuel gas from boilers may be accompanied with so-called "annex gases" which could be co-injected in a geological storage. These gases, such as SOx, NOx, or O$_2$ for instance, are likely to interact with reservoir fluids, rocks and well materials and could potentially affect the safety of the storage.

However, there are currently few data on the behavior of such gas mixtures, as well as on their chemical reactivity, especially in the presence of water. One reason for this lack comes from the difficulty in handling because of their dangerousness and their high chemical reactivity.

Therefore, the purpose of this work is to develop experimental and analytical protocols in order to acquire new thermodynamic data on the systems SO$_2$ + water and NO + water + salt under geological conditions of pressure and temperature. Acquisition of PVT experimental data on these systems is based on Raman spectroscopy coupled to capillary techniques and in situ analysis in autoclave, allowing to determine, in fine, solubilities of both SO$_2$ and NO in water and water + salt systems and co-solubilities of the water in the gas phase. This paper is devoted to very preliminary results validating the interest to perform further quantitative studies.
2. Experimental setup

2.1. Materials

Experiments are performed with deionized Milli-Q water (18.2 MΩ.cm). Seven salinities (NaCl, Sigma-Aldrich, \( \geq 98\% \) minimum purity) are tested: molalities of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 3.5 mol.kg\(^{-1}\).

Nitric oxide and sulfur dioxide gases were obtained from Alphagaz/Air Liquide with an overall purity of 99.9%. The initial pressure in the bottles doesn’t exceed several bars of pressure.

2.2. Fused silica capillary capsules (FSCCs)

FSCCs, purchased from Polymicro Technologies, have an internal diameter of 100 \( \mu \)m, an external diameter of 320 \( \mu \)m, and a length of approximately 1.5 cm. Capillary tubes were prepared following the method developed by [1] and is extensively described in [2].

Polyimide coating of the capillary tubes was burned before being sealed at one ending using a H\(_2\)-O\(_2\) microtorch (Elmaflame). Solutions are loaded from the open extremity. Samples are then centrifuged at 12000 rpm for 30s to transfer the solutions to the sealed end. The open extremity of the tube is connected to a stainless steel injection line for hazardous gases (Fig. 1). The vacuum is done in the line and in the fixed capillary tube. Capillary tube is then immersed into liquid nitrogen to freeze the water and pump residual air in the system. In a second step, capillary tube is pressurized with the wanted gases with a pressure of around 1 bar. Gases were trapped by condensation because after immersion of the capillary in the liquid nitrogen. Capillary tubes are sealed at the other end using the H\(_2\)-O\(_2\) microtorch.

2.3. Batch autoclave

In parallel, batch experiments are conducted in a 12 ml hastelloy autoclave equipped with a sapphire window (Fig. 2) allowing the Raman analysis at temperature and pressure up to 150°C and 200bar, respectively.

Autoclave is filled with 3 ml of deionized Milli-Q water (18.2 MΩ.cm). An oven coupled to proportional-integral-derivative controller (Toho TTM-004) is used to regulate the temperature of the system. The autoclave is connected to a gas line allowing the injection of gas at pressures up to 10 bar. To reach pressures up to 150bar, the autoclave is then directly connected to an argon tank (X50S Argon technical/AirProducts). The pressure in the system is obtained using a digital manometer (Leller LEO 2) with an accuracy of 0.1% FS.
2.4. Raman spectroscopy

Raman spectra on capillary capsules are acquired using a LabRAM HR spectrometer (Horiba Jobin Yvon) equipped with a 600 g mm$^{-1}$ grating and an edge filter. The excitation beam is provided by a Stabilite 2017 Ar+ laser (Spectra Physics, Newport Corporation) at 514.53 nm and a power of 400 mW, focused in the capillary using a $\times$ 20 objective (Olympus). Spectra were collected in the wavenumber interval between 100 cm$^{-1}$ and 4200 cm$^{-1}$. Spectra are obtained with 10 accumulations and with acquisition time between 1 and 10 s as a function of the samples, to have the maximum signal intensity between 1/3 and 2/3 of the CCD saturation level (i.e. 20000-40000 counts).

Measurements are performed first at 25°C and then up to 300°C. To allow measurements as a function of the temperature, the capillary is set on a dedicated heating-cooling stage (Linkam CAP500). Its position in the axis of the Raman microscope can be adjusted along the x and y direction by use of two micrometric screws. The Raman spectra are processed using Labspec© software.

For experiments in the batch autoclave, a RXN1 (Kaiser Optical Systems) spectrometer equipped with a Nd-YAG laser at 532 nm is used. A $\times$ 20 objective with a long focal distance and coupled to a Raman head is connected to the autoclave in front of the sapphire window. A total of 10 acquisitions of 5 seconds each is cumulated to provide a satisfactory spectrum (between 30000 and 40000 counts). Spectra are collected in the Raman shift interval between 100 cm$^{-1}$ and 4375 cm$^{-1}$. The Raman spectra are processed using iC Raman© software.

3. Results and discussion

3.1. Influence of salinity and temperature in the NO + water system

The influence of both temperature and salinity is studied using the fused silica capillary capsules (FSCCs).

Fig. 3 shows the Raman spectra (100-4200 cm$^{-1}$ range) recorded at room temperature in a capillary capsule in both gas and liquid phases (NO and aqueous solution). Assignments of major peaks are given in Table 1. In the gas phase, the NO peak is located at 1865 cm$^{-1}$ [4], [5], [6]. Peaks of N$_2$O with a weak intensity are visible at 1185 and 2222 cm$^{-1}$ [7], [8]. This is likely due to the disproportionation of NO to give N$_2$O and other byproducts in agreement with reactions (1) or (2).
$$4\text{NO} + \frac{1}{2} \text{H}_2\text{O} = 3/2 \text{N}_2\text{O} + \text{H}^+ + \text{NO}_3^-$$ (1)

$$2\text{NO} = \frac{1}{2} \text{O}_2 + \text{N}_2\text{O}$$ (2)

The reaction (2) is likely to occur since no nitrates are detectable in the solution. In addition, peaks N$_2$ (2335 cm$^{-1}$) and O$_2$ (1872 cm$^{-1}$) are present, due to atmosphere contamination and/or to disproportionation reactions such as (3).

$$2\text{NO} = \text{N}_2 + \text{O}_2$$ (3)

In the aqueous phase, peak at 1865 cm$^{-1}$, corresponding to aqueous NO, is detectable. Peaks of water, as expected, are located at 1650 cm$^{-1}$ (OH bending) and 3200 and 3400 cm$^{-1}$ (OH stretching).

<table>
<thead>
<tr>
<th>Group</th>
<th>Raman shift /cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH bending (H$_2$O)</td>
<td>1650</td>
</tr>
<tr>
<td>N$_2$</td>
<td>2335</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>1185-2222</td>
</tr>
<tr>
<td>NO</td>
<td>1865</td>
</tr>
<tr>
<td>O$_2$</td>
<td>1872</td>
</tr>
<tr>
<td>OH stretching (H$_2$O)</td>
<td>3200-3400</td>
</tr>
</tbody>
</table>

The influence of temperature is studied with experiments between 100 and 300°C by heating the capillary at constant volume.

As can be seen in Fig. 4, intensities of the H$_2$O band (OH stretching) become weaker at higher temperatures, while the intensity of the NO peak (1865 cm$^{-1}$) is relatively unchanged. The position of the OH stretching bands of water also changes according to the temperature, a rightward shift occurring when the temperature increases. The Table 2 sums up the positions of these peaks as a function of the temperature. This implies that a correct calibration of the peaks of water has to be performed to get semi-quantitative data of the concentration dissolved species.

<table>
<thead>
<tr>
<th>T°C</th>
<th>Raman shift /cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>3225</td>
</tr>
<tr>
<td>60</td>
<td>3229</td>
</tr>
<tr>
<td>890</td>
<td>3232</td>
</tr>
<tr>
<td>100</td>
<td>3234</td>
</tr>
<tr>
<td>150</td>
<td>3238</td>
</tr>
<tr>
<td>200</td>
<td>3243</td>
</tr>
<tr>
<td>250</td>
<td>3250</td>
</tr>
<tr>
<td>300</td>
<td>3267</td>
</tr>
</tbody>
</table>

The influence of salinity is studied by quantifying the peak areas of both NO and H$_2$O and representing them as their ratio A(NO)/A(H$_2$Odef). The experiments are carried out for pure water and salinities of 2 and 3 mol.kg$^{-1}$. 

![Fig. 4. Raman spectra in the aqueous phase in the system NO + H$_2$O + NaCl (2 mol.kg$^{-1}$) as a function of the temperature: 100C; 200C; 300C.](image-url)
Fig. 5. Raman peaks area ratio A(NO)/A(H$_2$O$_{def}$) for the system NO + H$_2$O + NaCl as a function of the temperature and the salinity: pure water; 2 mol.kg$^{-1}$ and 3mol.kg$^{-1}$ NaCl.

The area of the bending vibration band of water is measured between 1500 and 1800 cm$^{-1}$. The integration bounds of the dissolved NO peak is set in such a way that a straight baseline is tangent to the spectrum curve. Fig. 3 shows the evolution of the NO peak in the aqueous phase normalized to the water band at different temperatures and salinities. If we assume that the NO concentration is linearly linked to the peak area ratio, we can see that the NO concentration in solution is relatively constant for temperatures up to 100°C and then rapidly increases above 200°C. The salinity seems to increase the amount of dissolved NO but with a less marked tendency between 2 and 3 moles NaCl.

Because the experiments is isochoric, the increase of the temperature corresponds to an increase of the total pressure of the system that has to be considered for further quantification.

3.2. Batch autoclave

The Raman spectra of NO and SO$_2$ in H$_2$O are acquired at 30°C. In the case of NO and in our experimental conditions, the low solubility of the gas in water does not allow to put in evidence the existence of a peak of NO at pressures between 1 and 80 bar of total pressure. In the system SO$_2$ + H$_2$O, the SO$_2$ peak was measured at 1150 cm$^{-1}$ [9] at pressures between 3 and 8 bar.

Fig. 6. Raman spectra of dissolved SO$_2$ in aqueous solution at 30°C and as a function of the pressure: 3, 5 and 7 bar.

Fig. 6 shows the evolution of the Raman spectra of SO$_2$ in the aqueous phase as a function of the pressure. Increases of intensity of the SO$_2$ peak (1150 cm$^{-1}$) for pressures between 3 and 7 bar is related to the increase of the SO$_2$ solubility in the water. In order to validate a possible quantification by Raman spectrometry, the Raman data are correlated with experimental solubility data of the literature [10].
The Fig. 7 shows the expected SO$_2$ solubility as a function of the peak area ratio $A(SO_2)/A(H_2O)$. There is a positive but not linear correlation between the two parameters. This implies that a specific calibration has to be performed to get quantitative data of SO$_2$ solubility. The sensibility to the salinity will also be tested to study its influence on the possible SO$_2$ solubilization.

4. Conclusion

The purpose of this paper is to develop experimental and analytical protocols in order to acquire new thermodynamic data on SO$_2$ and NO containing systems under geological conditions of pressure and temperature.

The experimental based on fused silica capillary capsules (FSCC) which are transparent in the visible range, making possible the observation of the different phases, the quantification of their volume and the analysis of their chemical composition by Raman spectrometry to identify and quantify the molecular species of the fluid phases, but also the mineral phases resulting of possible chemical reactions (disproportionation, drying, etc.). These micro-reactors can be heated or cooled allowing the investigation of a large range of temperatures, from -190 to + 500°C. The geometry of the capsules (elongated shape, very low volume) makes possible to reach high gas pressures in the system, up to several kilobars, under safe working conditions.

The batch reactor has the advantage to control both the pressure and the temperature of the system. Its sapphire window allows performing Raman analyses of the fluid phases. Because initial SO$_2$ or NO provided by the industry cannot exceed several bars, the pressure in the reactor can only be increased with an inert gas, allowing only weak partial pressures of the desired gases.

The Raman analysis can provide both the solubility of the gases (SO$_2$ and NO) in water and the co-solubility of water in the gas phase, as well as the nature of the possible secondary phases (disproportionation reaction). A quantitative method to determine the concentration of the aqueous species will be developed through the implementation of a dedicated protocol, in particular by the realization of titrations of solutions of some acids (nitrous, nitric, sulphurous, sulphuric acids, etc.) coupled with Raman microspectrometry. The variation of the Raman peaks areas of the species of interest can calibrated according to the different physic-chemical parameters (P, T, pH, salinity). Different salinities are tested to determine, and in the future to quantify, their possible effects on the solubility of NO and SO$_2$. To investigate realistic conditions in the framework of the geological storage, temperature is varied between room temperature and 300°C. Because capillaries are closed systems, the fluid follows an isochoric evolution with temperature.

Finally, this study provides demonstrates that new thermodynamical data can be acquired from these original setups. These data are essential for predicting the behavior of the fluids, injected and initially present in the reservoir, under geological conditions of CO$_2$ storage on the short, medium and long term. These data will be useful to implement the numerical codes used to model the evolution of the storage during its life.

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References