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Thermodynamic study of mixtures of compounds present during the Carbon Dioxide Capture, Transport and Storage

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Abstract

Within the fight against global warming and the reduction of greenhouse-gases emission, research has been particularly intense over the last years to develop efficient processes of carbon dioxide captures. Indeed, along with carbon dioxide and water, a great number of compounds such as O₂, N₂, Ar, SO_x, NO_x, H₂ and CO can be present at different levels of concentration. The objective of this communication is to provide new sets of data to characterize phase equilibrium of these systems for the development of geological storage technologies. So, Isothermal vapour-liquid equilibrium data are reported for the following systems (SO₂-O₂-N₂ and CO₂-O₂-H₂O). The pressure and temperature ranges for this study are 6-18 MPa and 323-373 K, respectively. All measurements were carried out using an apparatus based on the “static-analytic” method.

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1. Introduction

The Intergovernmental Panel on Climate Change (IPCC) has stated that global greenhouse gases emissions should be reduced by 50 to 80 percent by 2050 [1]. The largest contributor among these gases is the carbon dioxide CO₂. One of the options for reducing atmospheric emissions of CO₂ from human activities (such as burning of fossil fuels) is the Carbon dioxide Capture and Storage (CSS). The CCS involves the capture, the transport and the storage into underground formations like deep saline aquifers or depleted oil and gas fields. Depending on the industrial sector (energy production, cement factory, refining, etc.) and on the type of capture process, the composition of gases accompanying CO₂ (also called contaminant gases) can considerably vary. Indeed, along with CO₂ and water, many other compounds such as O₂, N₂, Ar, SO_x, NO_x, H₂ and CO can be present at different levels of concentration in flue gases. The thermodynamic properties of CO₂ mixtures are essential for the design and the operation of CO₂ capture, transport and storage systems. For example, the Vapour-Liquid Equilibrium (VLE) of CO₂ mixtures is one of the parameters for designing purification processes in oxy-fuel combustion [2]. However, there are currently few data available in the open literature on the thermodynamic

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behaviour of these gas mixtures as for example CO₂-N₂ [3-13], CO₂-O₂ [4, 14], CO₂-Ar [15], CO₂-SO₂ [16-17], SO₂-N₂ [18-20], and SO₂-O₂ [18, 20]. This lack of experimental data must be coming from the difficulty in handling such compounds because of their dangerousness and their chemical reactivity.

In the present work, the thermodynamic behaviour of the following systems (SO₂-O₂-N₂ and CO₂-O₂-H₂O) was studied through experimental measurements, since, to the best of our knowledges no data are available in the open literature.

This article is organized as follows. Section 2 presents the experimental setup used to investigate VLE of the ternary mixtures. In section 3, we present and discuss our obtained data. This paper ends with a fourth section which gives our conclusions.

2. Experimental setup

2.1. Apparatus description

The apparatus used is based on the “static-analytic” method which was originally described by *El Ahmar et al.* [20]. The equilibrium cell (EC) placed inside an oven (O) (C3000, France Etuves), consists of a titanium body of about 80 cm³, and operates at maximum pressure and temperature of 25 MPa and 425 K, respectively. The body equipped with two sapphire windows (SW) holds two ROLSITM samplers [21] fixed on the top of the cell. One ROLSITM is used for sampling the liquid phase (LS) and the other one for the vapour phase (VS). Two pressure transducers (Druck, model PTX 611) and two platinum resistance thermometer probes (PP) are connected to the equilibrium cell. Three valves allow the evacuation, the cell loading and the degassing. The sample analysis is carried out by means of gas chromatography (GC). The system is stirred thanks to a variable speed stirrer. For the gas loading, there are two possibilities according to the target pressure: a direct connection to the gas bottle or a connection through a thermal compressor (TC).

2.2. Calibrations

Cell internal pressures are measured using two pressure transducers (Druck, model PTX 611): a high pressure transducer (HPT, maximum 20 MPa) which is always connected, and a low pressure transducer (LPT, maximum 4 MPa) which is isolated by the home made shut off valve (SV) when the pressure exceeds 4 MPa. The pressure transducers are thermally regulated by means of a PID regulator (TR, from WEST, model 6100) and are connected to a data acquisition unit (AOIP, France). The calibration is performed against a dead weight pressure balance (Desgranges & Huot 5202S, CP 0.3-40 MPa, Aubervilliers, France). Uncertainties are estimated to be within ± 0.2 kPa and ± 0.4 kPa for LPT and HPT, respectively. The two platinum resistance thermometer probes (100 Ω) are calibrated by comparison to a standard probe (25 Ω, TINSLEY) calibrated by the ‘Laboratoire National d’Essai’. They are coupled to a HP multi-meter. Uncertainties are estimated to be within ± 0.01 K for both probes. The signals from the probes (temperatures and pressures) are transmitted to a data acquisition system (DAS) which is connected to a PC via the Ltc10 interface and processed thanks to the PC. The thermal conductivity detector (TCD) of a Perichrom gas chromatograph (PR-2100) was calibrated using known amounts of compounds introduced through syringes. The column used for this analytical work is a Porapak Q, 80/100 mesh, 2 m *1/8” Silcosteel (Restek, France). Maximum uncertainties are estimated to be less than 2.8 % for both vapour and liquid mole fractions.

2.3. Experimental procedure

The experimental procedure for all measurements consisted of the following steps: evacuation of the equilibrium cell using a vacuum pump; introduction into the cell of given quantity (approximately 25 cm³) of the compound having the lowest vapor pressure (SO₂ or H₂O); setting of thermostat temperature; and introduction of a small quantity of the mixture (O₂-N₂ or CO₂-O₂). It was ensured that sufficient time was allowed for the system to reach thermodynamic equilibrium (temperature and pressure stabilization). Once it was deemed that the system was at equilibrium, sampling and analysis of liquid and vapor phases was initiated. In order to check for repeatability, which must be better than ± 1 %, several samples are successively withdrawn and analyzed. A new equilibrium is then produced by addition of the mixture. This procedure is continued until the whole composition range is covered. Once the determination of one isotherm is completed, the cell is emptied and the procedure repeated for a new isotherm.

3. Results

3.1. Vapour-liquid equilibrium data for the $\text{SO}_2\text{-O}_2\text{-N}_2$ mixture

After studying the thermodynamic behaviour of two SO_2 -containing binary mixtures, $\text{N}_2\text{-SO}_2$ [20], and $\text{O}_2\text{-SO}_2$ [20], the experimental VLE data of the $\text{SO}_2\text{-O}_2\text{-N}_2$ mixture were measured at 323.15, 343.15 and 373.15 K for three pressures (11, 15 and 18MPa). All the considered temperatures are below the critical temperature of SO_2 (430.75 K). In this paper, only one result is presented (Fig 1). The $\text{SO}_2\text{-O}_2\text{-N}_2$ mixture corresponds to a type I phase diagram in the Weinstock classification [22].

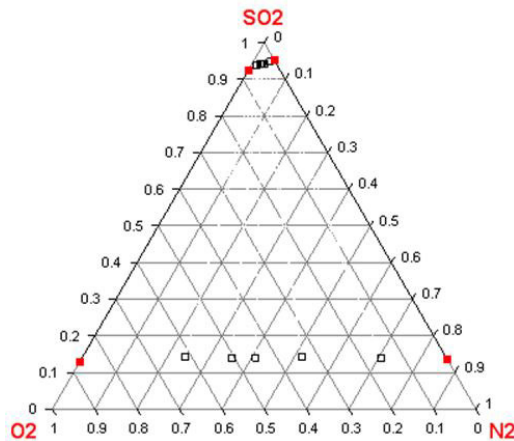


Fig. 1. Phase diagram of $\text{SO}_2\text{-O}_2\text{-N}_2$ mixture. Full symbols correspond to binary data and empty symbols correspond to ternary data (11 MPa - 323.15 K)

3.2. Vapour-liquid equilibrium data for the $\text{CO}_2\text{-O}_2\text{-pure H}_2\text{O}$ mixture

The (CO_2/O_2) gas mixture at different compositions of oxygen (1.5, 3, 6 and 10%) has been studied in presence of pure water at 363.15 K and at five pressures (6, 8, 10, 12 and 15 MPa). The results obtained are presented in Figure 2. The solubility of CO_2 increases with pressure at constant temperature. While increasing the composition of oxygen in the (CO_2/O_2) gas mixture, the mole fraction of CO_2 decreases (Figure 2).

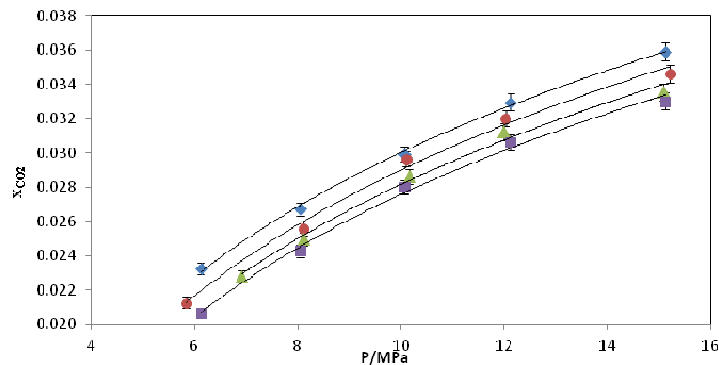


Fig.2. Mole fraction of CO_2 as function as the pressure at 363.15 K for the $\text{CO}_2\text{-O}_2\text{-pure H}_2\text{O}$ mixture \blacklozenge 1.5% \bullet 3% \blacktriangle 6% \blacksquare 10% : O_2 composition in the (CO_2/O_2) gas mixture.

3.3. Vapour-liquid equilibrium data for the $\text{CO}_2\text{-O}_2\text{-saline H}_2\text{O}$ mixture

The (CO₂/O₂) gas mixture (4% of O₂) has been studied in presence of saline water at 363.15 K and at five pressures (6, 8, 10, 12 and 15 MPa). The salinity of water used is 30g/L of sodium chloride. The results obtained are presented in Figure 3. Since, we did not determine the solubility of CO₂ in pure water at this composition of O₂, an empirical model based on the previously measured data has been established and given in equation 1:

$$x_{CO_2} = -9 \times 10^{-5} P^2 + 0.0037 P + 0.0036 \tag{eq. (1)}$$

Where P is the pressure

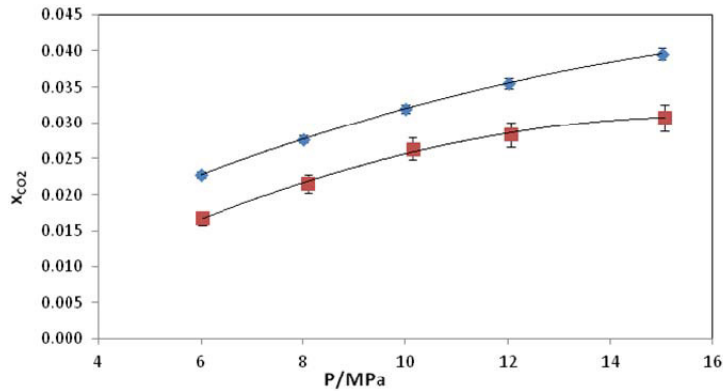


Fig.3. Mole fraction of CO₂ as function as the pressure at 363.15 K for the CO₂-O₂-H₂O mixture (4% of O₂ in the (CO₂/O₂) gas mixture. ♦ pure water; ■ saline water .

We noticed that the CO₂ is less dissolved in saline water than in pure water. This decrease is related to the Salting-Out effect (S.O.) [23], which can be expressed as a follow (eq.2):

$$\% S.O. = 100 * (x_0 - x) / x_0 \tag{eq. (2)}$$

Where x₀ and x are the mole fractions of CO₂ in pure water and saline water, respectively.

It seems that the salting-out effect on CO₂ attains a minimum at 10 MPa and increases at higher pressure.

Table 1: Salting-out effect on CO₂ as function of pressure

P (MPa)	% S.O.
6	26
8	22
10	18
12	20
15	22

4. Conclusion

In the context of the reduction of greenhouse gas emissions reduction, CO₂ capture process constitutes one of the main problems to handle. The degree of purity of the captured CO₂ is a key factor for transportation, injection and sequestration. Contaminant gases are taken into account in industrial processes of capture but, as mentioned before, they remain poorly studied for the development of geological storage technologies.

The work performed here provides new sets of data to characterize phase equilibrium of systems including CO₂ co-injected gases such as SO₂, O₂ and N₂ and water (pure or saline) in order to improve our understanding of their possible geological storage with CO₂.

The next step of this work is to continue generating reliable and accurate experimental data (Vapour-Liquid Equilibrium, solubility in saline water, density, etc...) over a wide range of pressure and temperature conditions and also to develop and validate correlations and thermodynamic models able to represent correctly the collected data.

Acknowledgements

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