Fluid Phase Equilibria 423 (2016) 156–171

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Densities and derived thermophysical properties of the 0.9505 $CO_2 + 0.0495\ H_2S$ mixture from 273 K to 353 K and pressures up to 41 MPa

Mahmoud Nazeri [a], Antonin Chapoy [a, b, *], Alain Valtz [b], Christophe Coquelet [b], Bahman Tohidi [a]

[a] Hydrates, Flow Assurance & Phase Equilibria Research Group, Institute of Petroleum Engineering, Heriot-Watt University, Edinburgh EH14 4AS, UK
[b] MINES ParisTech PSL Research University, CTP-Centre of Thermodynamics of Processes, 35, Rue Saint Honoré, 77305 Fontainebleau, France

A R T I C L E I N F O

Article history:
Received 2 March 2016
Received in revised form
8 April 2016
Accepted 24 April 2016
Available online 26 April 2016

Keywords:
Density measurement at high pressure
Carbon capture transport and storage
CO_2 and H_2S
Thermophysical properties
Acid gas injection

A B S T R A C T

From the development of sour reserves and acid gas injection into oil reservoirs to the impact of hydrogen sulfide in CCS scheme, knowledge of the phase behaviour and thermophysical properties of the hydrogen sulfide + carbon dioxide is essential. Due to the toxicity of CO_2 - H_2S system, there are few experimental data available in the literature. The aim of this work is to investigate the densities and thermodynamic properties of acid gases and liquids. Densities of the 95.05 mol% CO_2 + 4.95 mol% H_2S binary system were measured continuously using a high temperature and pressure Vibrating Tube Densitometer (VTD), Anton Paar DMA 512 at pressures up to 41 MPa at five different temperatures, 273, 283, 298, 323 and 353 K in gas, liquid and supercritical regions. The specific heat capacity, compressibility factor, dew point and bubble point of the system have also been derived from the measured density data. The experimental data then were employed to evaluate the GERG-2008 equations of state and classical cubic equations of state (PR, SRK and VPT) with a CO_2 volume correction model as well as volume translation.

1. Introduction

One of the most common impurities in natural gas is carbon dioxide. Most reservoirs around the world contain carbon dioxide. For instance, one of the biggest sour gas resources in Prudhoe Bay Alaska with more than 20 trillion cubic feet associated gas (with the oil) contaminated roughly by 12 mol% carbon dioxide and over 10 ppmv hydrogen sulfide. Similar acid gas content can be found in the Tangguh field in the South-East Asia, Indonesia. The In Salah gas field in Algeria also contains around 10 mol% CO_2. In the Middle East, there are some sour gas fields typically containing 3 mol% H_2S and 5 mol% CO_2. A comprehensive survey by Weeks et al. [1] shows that acid gas content composition can span from a few ppm to 90 mol% for carbon dioxide and from 0 to 60 mol% for hydrogen sulfide.

CO_2 content in natural gas pipelines should not be more than a specific amount which is typically 2–2.5 mol%. Any extra carbon dioxide from natural gas reservoirs, therefore, should be first removed and then transported to either re-injection to oil fields for enhanced oil recovery or should be stored in a depleted formations (e.g., Sleipner field [2] in the Norwegian North Sea or aquifer in In Salah gas field [3] in Algeria).

Sour gas and oil fields contain CO_2 and H_2S which should be removed from the produced oil or gas before sending to markets [4]. The desulphurisation process is costly and acid gas injection is seen as an alternative environmentally friendly method to deal with the toxic acid gases [5]. In the sweetening process of natural gas or oil produced, H_2S and CO_2 can be removed by different processes, e.g., using amine. The gas off the amine regenerator can be transported by pipelines to an injection well to be stored in geological basins [6]. The knowledge of phase equilibria [7,8] and thermophysical properties [9] of acid gases and liquids, particularly density [10], are essential to the design considerations of acid gas injection schemes [11,12].

CCS technology can provide a potential to cut/reduce the large

* Corresponding author. Hydrates, Flow Assurance & Phase Equilibria Research Group, Institute of Petroleum Engineering, Heriot-Watt University, Edinburgh EH14 4AS, UK.
E-mail address: Antonin.chapoy@pet.hw.ac.uk (A. Chapoy).

http://dx.doi.org/10.1016/j.fluid.2016.04.024
0378-3812/

Table 1
Details of the chemicals, suppliers and purities of the components used in this study.

Chemical name	Source	Initial purity[a]	Certification	Analysis method[b]
H_2S	Air Liquide	0.995 vol	Air Liquide Certified	SM
CO_2	Air Liquide	0.99995 vol	Air Liquide Certified	SM

[a] No additional purification is carried out for all samples.
[b] SM: Supplier method.

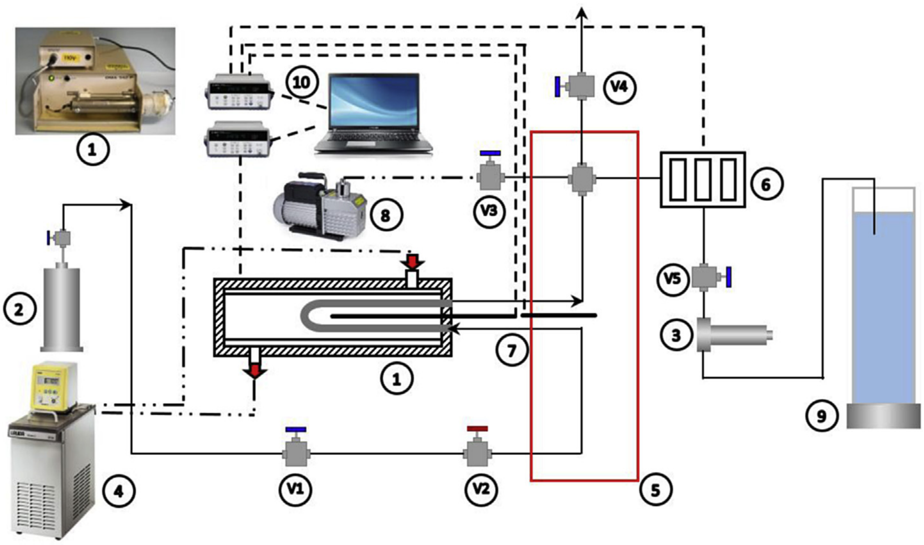

Fig. 1. Schematic diagram of the densitometer apparatus. 1) Anton Paar DMA 512 densitometer, 2) High pressure fluid vessel, 3) Capillary Valve (ROLSI™) [55], 4) Lauda liquid bath, 5) Liquid bath of circuit, 6) Pressure transducers, 7) Temperature probes, 8) Vacuum pump, 9) Neutralisation column, 10) Data acquisition unit, V1) Circuit valve, V2) Flow controlling ball valve, V3)Vacuum valve, V4) Venting valve, V5) Neutralisation valve.

scale release of CO_2 emissions. The process comprises three main steps: capture, transport and storage. Three capturing technologies are under development: pre-combustion, post-combustion and oxy-fuel combustion. The aim of each capturing technology is to capture CO_2, preventing it from release to the atmosphere, following this to transport it to a suitable place of storage. However, the CO_2 coming from capture processes will contain a range of impurities as none of the technologies are efficient enough to produce pure CO_2 [13]. The concentration and type of the impurities will depends on many factors like fuel type, capture technology and the design of the plant [14]. The presence of impurities changes thermophysical properties of the stream such as density, viscosity, specific heat capacity, compressibility and critical pressure, which can have a significant effect on the hydraulic behaviour of the CO_2 stream [15].

To understand thermodynamic properties of different CO_2-mixtures, study of Equations of State (EoS) is extremely important. In literature several references are available on EoS suitable/used for CO_2 and CO_2 mixtures [16–19], nevertheless a suitable equation of state for mixtures in appropriate conditions for pipeline transport, in particular with a high CO_2 concentration, has not been clearly defined [20].

The pressure-volume-temperature behaviour, thermal properties and densities of sour gas/liquid mixtures are essential to proper design of sour natural gas processing units, CO_2 transport and injections as well as CCS scheme.

In this communication, new density data are presented for the 0.0495 H_2S + 0.9508 CO_2 binary system. In total, five sets of isothermal density data have been measured at 273, 283, 298, 323 and 353 K and pressures up to 41 MPa. The new experimental data are compared to literature data and predictions using the Peng-Robinson (PR-ES) [21], Soave-Redlich-Kwong (SRK-EoS) [22], Valderrama modification of the [23] Patel-Teja (VPT-EoS) [24] equations of state. The CO_2 volume correction [25] and Peneloux volume translation [26] have been introduced to these equations of state to improve the density prediction. Finally, apart from the cubic equations of state, the GERG-2008 EoS [27] which a wide-range multi parameter equation of state proposed, has also been evaluated using the new experimental data.

2. Literature review

Despite the importance of the volumetric behaviour of acid gases and liquids, due to the toxicity of the system, limited experimental data are available in the literature on the density of CO_2-H_2S binary systems. The first study on the pressure-volume-temperature behaviour of the CO_2-H_2S systems has been conducted by Bierlein and Kay [28] for the saturated states of eight mixtures of CO_2-H_2S from 273.15 K to the critical temperature of hydrogen sulfide. Mole fractions of CO_2 in this study are 0, 0.0630, 0.1614, 0.2608, 0.3759, 0.4728, 0.6659, 0.8292, 0.9009 and 1. Sobocinski and Kurata [29] experimentally studied the CO_2-H_2S systems at lower temperatures, i.e., below 273.15 K, to extend the data obtained by Bierlein and Kay [28]. They studied seven mixtures from the solid-liquid-vapour region to the critical region. A research report from the Gas Processors Association about thermodynamic properties of CO_2-H_2S mixtures [30] includes density measurements for four mixtures. The systems studied by Kellerman et al. [30] were 93.93 mol% CO_2 + 6.07 mol% H_2S, 90.45 mol% CO_2 + 9.55 mol% H_2S, 70.67 mol% CO_2 + 29.33 mol% H_2S and 50.01 mol% CO_2 + 49.99 mol% H_2S. They performed Burnett and Burnett-isochoric measurements for each mixture at temperatures