Hydrate Mitigation in Sour and Acid Gases

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ABSTRACT

While global demand for energy is increasing, it is mostly covered by fossil energies, like oil and natural gas. Principally composed of hydrocarbons (methane, ethane, propane...), reservoir fluids contain also impurities such as carbon dioxide, hydrogen sulphide and nitrogen. To meet the request of energy demand, oil and gas companies are interested in new gas fields, like reservoirs containing high concentrations of acid gases.

Natural gas transport is done under high pressure and these fluids are also saturated with water. These conditions are favourable to hydrates formation, leading to pipelines blockage. To avoid these operational problems, thermodynamic inhibitors, like methanol or ethanol, are injected in lines.

It is necessary to predict with more accuracy hydrates boundaries in different systems to avoid their formation in pipelines for example, as well as vapour liquid equilibria (VLE) in both sub-critical regions. Phase equilibria predictions are usually based on cubic equations of state and applied to mixtures, mixing rules involving the binary interaction parameter are required. A predictive model based on the group contribution method, called PPR78, combined with the Cubic – Plus – Association (CPA) equation of state has been developed in order to predict phase equilibria of mixtures containing associating compounds, such as water and alcohols.

To complete database for multicomponent systems with acid gases, VLE and hydrate dissociation point measurements have been conducted.

The developed model, called GC-PR-CPA, has been validated for binary systems and applied for different multicomponent mixtures. Its ability to predict hydrate stability zone and mixing enthalpies has also been tested. It has been found that the model is generally in good agreement with experimental data.

A mes parents

A ma sœur Stéphanie et mon frère Lucas

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INTRODUCTION

La demande en énergies fossiles ne cesse de s'accroitre avec l'augmentation de la population mondiale et l'émergence économique de nouveaux pays. Les industries pétrolières et gazières sont confrontées à de nouveaux défis : forage en mer profonde, sources non-conventionnelles et gaz acides (dioxyde de carbone et le sulfure d'hydrogène présents en quantités variables dans le gaz naturel). En plus de ces défis technologiques, les énergies fossiles sont aussi émettrices de dioxyde de carbone, gaz à effet de serre qui a un impact non négligeable sur le climat. Une des solutions serait de le capturer et le transporter vers des zones de stockage. Qu'il s'agisse du transport du gaz naturel ou du dioxyde de carbone, de l'eau peut être présente introduisant un risque supplémentaire : la formation d'hydrates de gaz. C'est sur cette problématique que s'appuie cette thèse. Un travail de modélisation a été effectué pour prédire les diagrammes de phases des hydrocarbures, des gaz acides (CO_2, H_2S) et inertes (N_2, H_2) en présence d'eau et d'alcools. Des études expérimentales ont été menées sur des systèmes multi-constituants pour évaluer la capacité du modèle à prédire les équilibres entre phases pour des mélanges complexes et le valider.

With the growing population and the economic emergence of new countries, the demand in fossil energies is continuously increasing. To meet the demand, oil and gas industries are looking to new types of reservoirs, and therefore face new challenges: deepwater drilling, unconventional oil and gases, acid gases (gases with an important concentration of carbon dioxide and hydrogen sulphide). In addition to these challenges, combustion of fossil fuels is the principal anthropological source of carbon dioxide emissions to the atmosphere. It is considered as the major cause of global warming. A solution proposed is to capture, transport and store carbon dioxide produced in suitable geological reservoirs.

Whether natural gas or carbon dioxide, they are transported with impurities. One of them is water, which may lead to hydrate formation in pipelines. This introduces a serious flow assurance issue, since hydrates may block pipelines.

Chapter 1 presents natural gas and carbon dioxide transportation. The thesis is principally focused on hydrate formation during transportation. Since the systems of interest contain acid gases, it leads to different problems, which may be encountered during transportation. In the presence of water, they intensify the risk of pipeline corrosion and blockage (hydrates formation). To avoid hydrates formation, inhibitors such as methanol, ethanol or glycols are used. Therefore accurate knowledge of mixtures phase equilibria are important for safe operation of pipelines and production/processing/separation facilities.

As part of three industrial projects experimental measurements have been conducted and presented in Chapter 2:

- Hydrate dissociation points and vapour-liquid equilibrium points have been measured for different mixtures to determine the impact of aromatic impurities on acid gas systems, in the case of acid gas injection.
- Hydrate dissociation points of rich CO_2 systems have been also measured in the context of carbon dioxide transport in Carbon Capture and Storage (CCS)
- Hydrate dissociation points of different hydrocarbon mixtures in the presence of hydrate inhibitors have been determined in the context of flow assurance

Data generated are used to evaluate and validate the capability of the model to predict phase equilibria of complex systems.

Phase equilibria are predicted with thermodynamic models. Cubic equations of state (EoS), such as the Soave-Redlich-Kwong (SRK EoS) **[1]** and the Peng-Robinson (PR EoS) **[2]** equations of state are widely used in the industry. But they are limited for mixtures containing associating compounds, i.e. forming hydrogen bonding, such as water or alcohols, because they have been developed mainly for hydrocarbons. To improve their ability to predict phase behaviour, none zero binary interaction parameters are introduced. They are adjusted on experimental data for each binary system of interest. In the case of no data are available, there are two solutions: or experimental data are conducted to complete database, or predictive models are used. One of the predictive model available in the literature, the PPR78 model **[3]**, is presented in Chapter 3, as well as the Cubic-Plus Associtaion EoS **[4]**, suitable for systems containing associating compounds.

In this thesis, a predictive model (called GC-CPA-PR, for Group Contribution – CPA – PR), combining the CPA EoS and the PPR78 model, has been developed and is explained in Chapter 4. The aim is to take into account the hydrogen bonding with the CPA EoS and to have a robust model to predict phase equilibria (VLE, LLE and hydrate stability zone) of different mixtures. Parameters have been adjusted for binary systems with associating compounds (water and alcohols) on experimental data taken from the literature.

Chapter 5 presents the validation of the model. First, predictions are compared to experimental data (VLE and LLE) taken from the literature for binary systems of water and alcohols. Then, the ability of the model to predict phase equilibria of more complex systems is assessed. Finally, the model is tested on hydrate stability zone and enthalpy of mixing predictions. The mixtures are either from the literature or those generated in laboratory and presented in Chapter 2.

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CHAPTER 1 – NATURAL GAS AND CARBON DIOXIDE TRANSPORT: PROPERTIES, FEATURES AND PROBLEMS

La consommation en énergies fossiles représente 80% **[1.1]** *de la consommation mondiale en énergies, avec une augmentation de la demande en gaz naturel. Pour répondre à cette demande, les industries s'orientent vers de nouvelles ressources, comme les gaz de schistes ou les gaz naturels à forte teneur en gaz acides. Ces derniers représentent 40% des ressources connues actuellement. Ils contiennent en proportions variables mais conséquentes du dioxyde de carbone et du sulfure d'hydrogène. Or ces composés sont des impuretés qu'il faut séparer des hydrocarbures pour répondre aux exigences techniques nécessaires avant toute commercialisation et utilisation. Il faut donc connaitre les différentes propriétés du gaz naturel pour adapter les conditions de transport.*

L'émission de gaz à effet de serre est à l'origine du réchauffement climatique. Les sources anthropiques en sont la principale cause, avec une part importante due à la combustion des énergies fossiles. Les émissions en dioxyde de carbone issues de l'industrie en sont une part non négligeable. Une des solutions étudiées est la capture du dioxyde de carbone et son stockage dans des sites géologiques. Quelque soit la technique de capture, le dioxyde de carbone est récupéré avec des impuretés, qui ont une influence non négligeable sur les propriétés du mélange.

Dans le cas de l'industrie gazière, l'eau est une des plus importantes impuretés à traiter. Elle est aussi présente en quantités variables avec le gaz naturel ou le dioxyde de carbone. En présence de gaz acides et d'un milieu aqueux, les pipelines peuvent se corroder. Le matériau étant détérioré, cela peut être une cause de fuite. La présence d'eau et de petites molécules (méthane, dioxyde de carbone, sulfure d'hydrogène…), dans certaines conditions de pression et de température, est une situation favorable à la formation d'hydrates. Ces structures cristallines peuvent bloquer les pipelines. Le sujet de cette thèse étant centré sur les hydrates de gaz, un rapide descriptif de la corrosion est donné dans la dernière partie avant de décrire plus en détails les caractéristiques des hydrates.

1.1. INTRODUCTION

The twentieth century has seen an important increase of the fossil energy demand with an annual growth rate for the natural gas of 3% for 30 years **[1.2]**. They represent today 80% of world energy consumption **[1.1]**. Figure 1.1 and Figure ***1.2*** show the world oil and gas production and consumption between 1987 and 2012. According to the US Energy Information Administration (EIA) the total world energy use is supposed to rise from 524 quadrillion British thermal units (Btu) in 2010 to 820 quadrillion Btu in 2040 **[1.3]**.

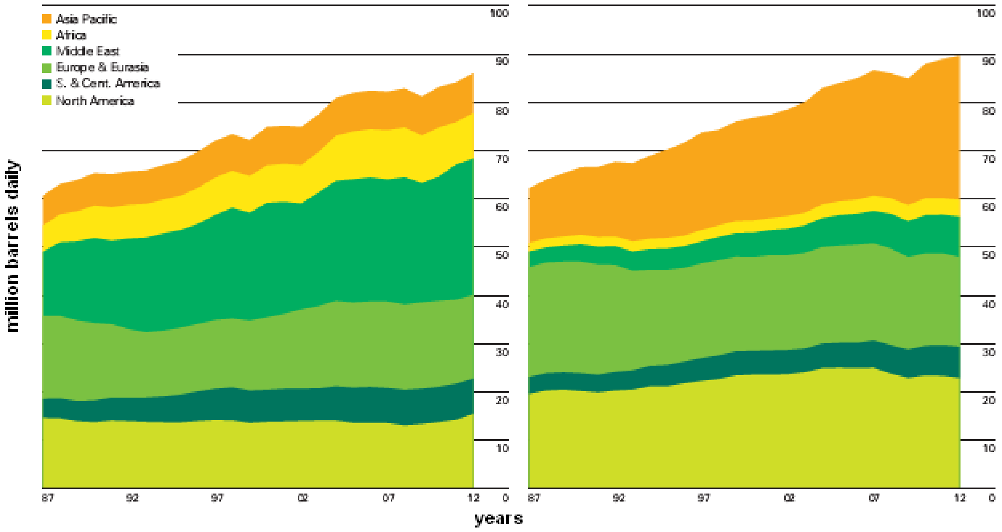

Figure 1.1: World oil production (left) and consumption (right) between1987 and 2012 **[1.4]**.

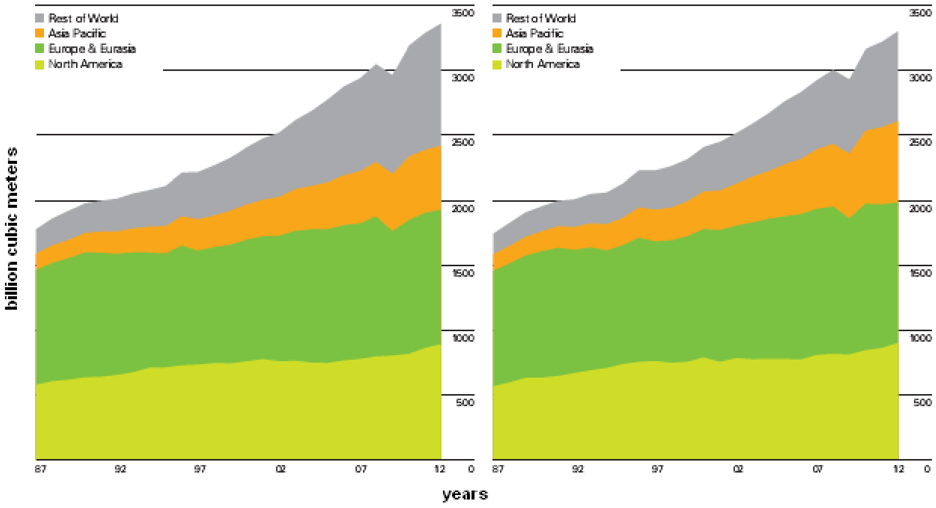

Figure 1.2: World Natural Gas production (left) and consumption (right) between1987 and 2012 **[1.4]**.

With the growing population, the demand is still increasing: the EIA foresees a 56% raise in the world energy consumption between 2010 and 2040 (Figure 1.3). This trend is strongest in countries outside the Organization for Economic Cooperation and Development (OECD) with a rise of 90%, while it is just 17% in OECD countries. Moreover, world industrial sector and transport consume half of the energies produced. Despite a decrease of liquid fuels use and an increase of renewable energies and nuclear plant use (plus 2.5 % per year), fossil fuels continue to supply the majority of the world energy demand. Indeed, liquid fuels are the most used in the transport sector and despite of the increasing prices, their used is supposed to rise by 38% from 2010 to 2040.

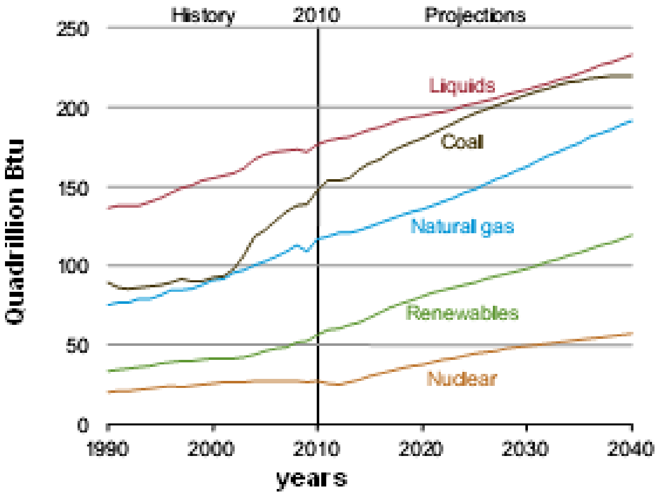

Figure 1.3: World energy consumption by fuel type between 1990 and 2010 and projections for the next 30 years **[1.3]**.

According to the EIA, natural gas use increases by 1.7% per year. With 116 quadrillion Btu consumed in 2010, the increase is estimated at 64 % with a consumption of 190 quadrillion Btu in 2040. Among all fossil energies, natural gas presents a lot of benefits: low risk since it is not toxic, lower carbon dioxide emissions relative to other fossil fuels and quicker reaction to demand peaks. With the consumption pace, the actual proven reserves (Figure 1.4) are supposed to be enough for 60 years. Oil and gas companies are interested in new gas fields, like shale, coal bed, tight and sour gas.

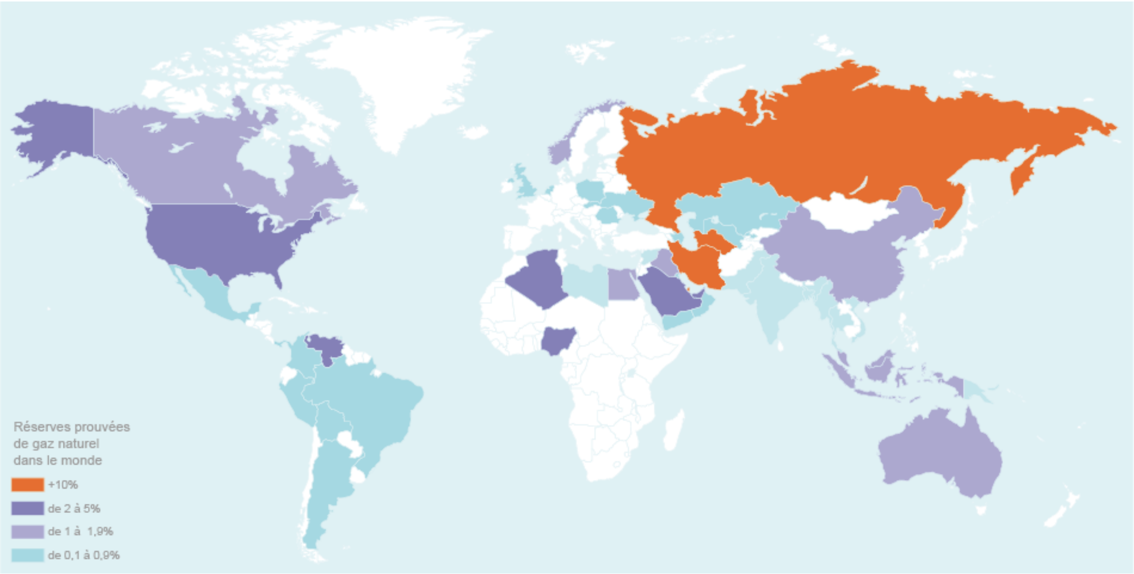

Figure 1.4: World Natural Gas reserves at the end of 2011 **[1.5]**. ■ *+10%,* ■ *from 2 to 5%,* ■ *from 1 to 1.9%,* ■ *from 0.1 to 0.9%*

40% of these reserves **[1.6]** are acid and sour gases (Figure 1.5), i.e. the percentage of carbon dioxide and hydrogen sulphide is significant. Middle Eastern and central Asian countries have the most important fields. Their production and transport can be a challenge, due to their corrosiveness in the presence of water, leading to pipelines damages and H_2S toxicity. Oil and gas companies are in search of environmentally friendly and gainful methods for dealing with acid and sour gases, as well as low energy consumption.

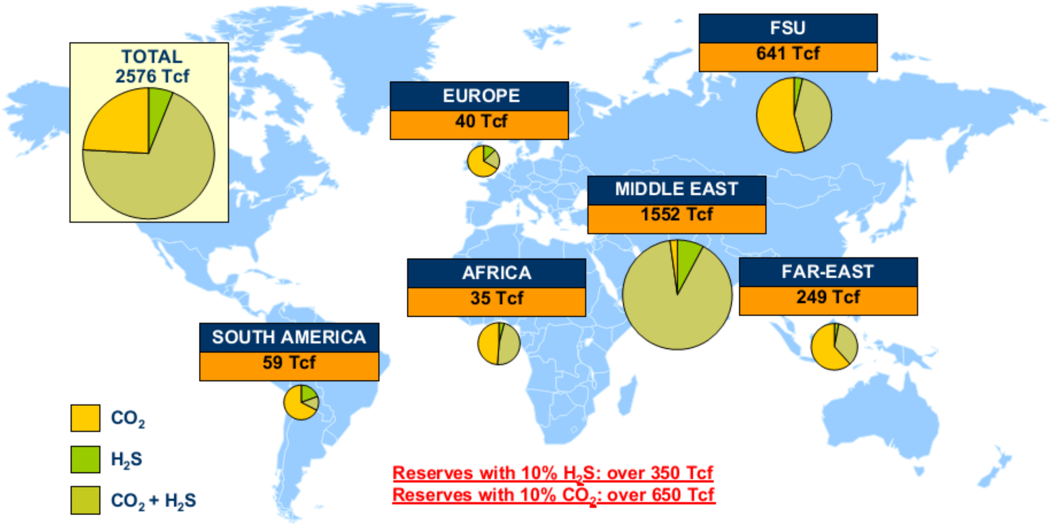

Figure 1.5: World sour and acid gas reserves **[1.7]**.

Some fields are even ultra-sour, with over 20% of CO_2 or H_2S. In all cases, these compounds are considered as impurities as well as water usually present in the reservoirs and other elements (e.g. nitrogen, helium...). They are removed by chemical absorption in separation units. Acid gases are commonly removed with different types of amines. For example, the maximum concentration of hydrogen sulphide allowed in treated gas is about 4 ppm **[1.8]**. They are then compressed and injected into suitable underground formations.

As a result of world's dependence on fossil energies, the release of carbon into atmosphere is increasing and leads to climate changes. The combustion of fossil fuels generates about 30 gigatons of CO_2 per year, or 43% of total CO_2 emissions **[1.9]**. In 2012, Coal represents 43% of total fuel-based CO_2 emissions, oil 33% and natural gas 18% **[1.10]** (see Figure 1.6).

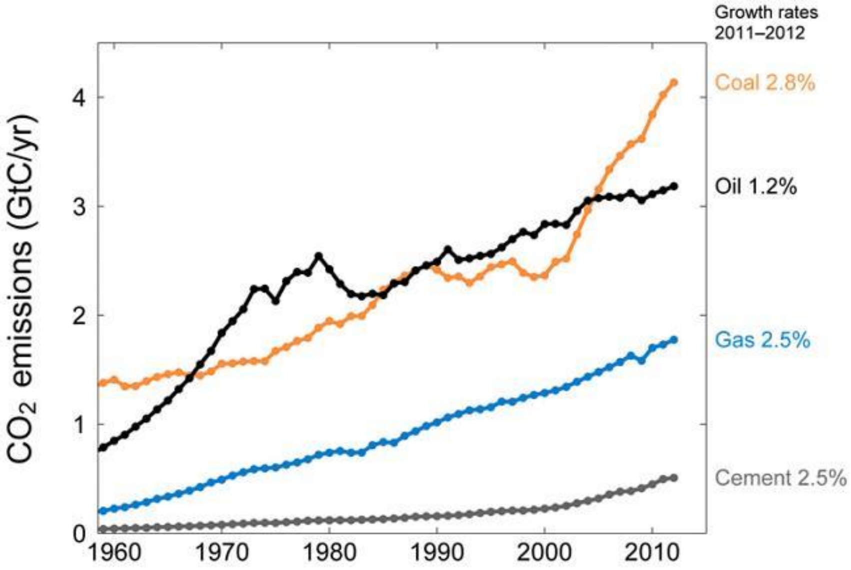

Figure 1.6: Global CO_2 emissions from fossil energies from 1960 to 2012 **[1.10]**.

Estimations predict an increase of temperature between 1.0 to 2.1°C per 3600 gigatons of CO_2 emitted **[1.11]**. Even if a solution is found now to stop carbon dioxide emissions, the climate changes are irreversible and last up to 1000 years **[1.12]**. Fossil energies-based CO_2 emissions come from both stationary (e.g. power plant, refinery) and non-stationary systems (e.g. urban transport) **[1.9]**. Different ways to reduce CO_2 emissions in the atmosphere have been proposed. One of the most promising is the Carbon Capture and Storage (CCS). Amines are currently used as chemical solvent in fuel process plants to remove carbon dioxide. But all carbon dioxide capture technologies, existing or future, depend on different factors:

- What kind of system (stationary or non-stationary)?

- CO_2 concentration in the gas mixture
- Presence of impurities (water, SO_x, NO_x...)?
- Temperature and pressure conditions

Then carbon dioxide is transported through pipelines for Enhanced Oil Recovery (EOR), which looks to be the main target for many operators, or to storage sites. The ones actually considered are geologic formations (deep saline aquifers, depleted oil and gas fields...) **[1.9]**.

Whether in natural gas production, carbon dioxide capture or acid gas injection, water may be present. During the different steps in production, transportation and processing, changes in temperature and pressure can lead to water condensation, ice and/or gas hydrates formation.

General information of both natural gas and carbon dioxide, as well as their transportation conditions are presented below. Origins of water, corrosion problem and hydrate formation in pipelines are also explained.

1.2. NATURAL GAS TRANSPORT

1.2.1. What is Natural Gas?

If a natural substance is in gaseous state at IUPAC standard conditions[1], it is a **permanent gas**. In subsurface rock reservoirs it is hydrocarbons from methane to butane, carbon dioxide, nitrogen, hydrogen sulphide, hydrogen, helium and argon **[1.8]**. But the natural gas recovered, contains permanent gases but also heavier hydrocarbons. Compositions depend on reservoir source, history and present conditions. An example of typical composition is given in Table 1.1.

Table 1.1: Example of natural gas composition **[1.13]**

Components	Composition [mole %]
Methane	84.07
Ethane	5.86
Propane	2.20
i-Butane	0.35

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[1] Air at 273.15 K and 10^5 Pa

Table 1.1 (to be continued): Example of natural gas composition **[1.13]**

Components	**Composition [mole %]**
n-Butane	0.58
i-Pentane	0.27
n-Pentane	0.25
n-Hexane	0.28
n-Heptane and heavier	0.76
Carbon dioxide	1.30
Hydrogen sulphide	0.63
Nitrogen	3.45

The proportion of carbon dioxide, hydrogen sulphide and nitrogen depends on the reservoir. For example, there is 15 % of hydrogen sulphide in the reservoir in Lacq (France), but 87 % in Alberta (Canada).

1.2.1.1. Origin of Natural Gas

As seen above, natural gas is composed of hydrocarbon and non-hydrocarbon compounds. Hydrocarbons result from organic decomposition in two different modes **[1.8]**.

- The first one is the bacterial gas. It is formed in recent sediments, formed from the accumulation of marine muds. Bacteria affect the decomposition of organic remains during the deposition of sediments. Methane is the only hydrocarbon formed, and derives from the reaction (R-1.1).

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \tag{R-1.1}$$

  Carbon dioxide is dissolved in water naturally present in reservoirs. Hydrogen results from the other bacteria. Suitable conditions are required for this reaction: the temperature must be lower than 338.15 K, which is encountered at a depth between 2000 and 25000 m, and in an environment without free oxygen.

- The second one is the thermal gas. In an environment without oxygen, the organic matter is slowly degraded, according to a set of kinetic equations of order 1 under the following form (Equation (1.1)).

$$\frac{dX_i}{dt} = -kX_i \tag{1.1}$$

  with k the activation energy following the Arrhenius law[2] and X_i the concentration of the compound considered.

  Residues of the decomposition are not soluble in organic solvents and form the kerogen. With the evolution of the sedimentary basins, sediments are buried deeper: the increase of temperature (between 50 to 110 °C) leads to a thermal degradation of the kerogen. In this case, it produces hydrocarbon and non-hydrocarbon compounds (CO_2, H_2O, H_2S, H_2, N_2).

1.2.1.2. Natural Gas Resources

Gas reservoirs are classified into two categories: “conventional” and “non-conventional” reservoirs. The conventional ones are mainly those operated today. The different types of non-conventional reservoirs are listed below **[1.13]**:

- *Gas in tight sand* is generally in formation having porosities of 0.001 to 1 millidarcy (md). At higher permeabilities, conventional fracturing is used;
- *Gas in tight shales*: the shale is fissile, finely laminated and varicoloured. Permeability is less than 1 md;
- *Coal-bed methane* is gas in minable coal beds with depths less than 914.4 meters. The production of this type of gas may be limited regarding to practical constraints;
- *Geopressured reservoirs* at abnormally pressured reservoirs;
- *Methane gas hydrates* are naturally present throughout the world, in seabeds and in some permafrost regions. It is considered as a future unconventional gas resource.

They are considerable, but they are underexploited for technical and economical reasons.

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[2] $k = Ae^{\frac{-E_a}{RT}}$

1.2.1.3. Natural Gas Properties

Phase diagrams are essential for the processing of natural gases and the design of transportation facilities. They show the state of the gas at different temperature and pressure conditions. For example, conditions of the formation of a liquid phase in process conditions can be seen on a phase diagram of the system considered. Therefore it is possible to distinguish different types of gases in the context of production:

- *Dry gas*: no liquid phase is formed in the conditions of the production;
- *Humid gas*: a liquid phase is formed during the production in surface conditions;
- *Gas condensate*: a liquid is formed during the production in the reservoir;
- *Associated gas*: the gas coexists with oil. Associated gas occurs both in the gaseous phase above the oil phase and dissolved in the oil phase.

An example of a phase diagram is given in Figure 1.7.

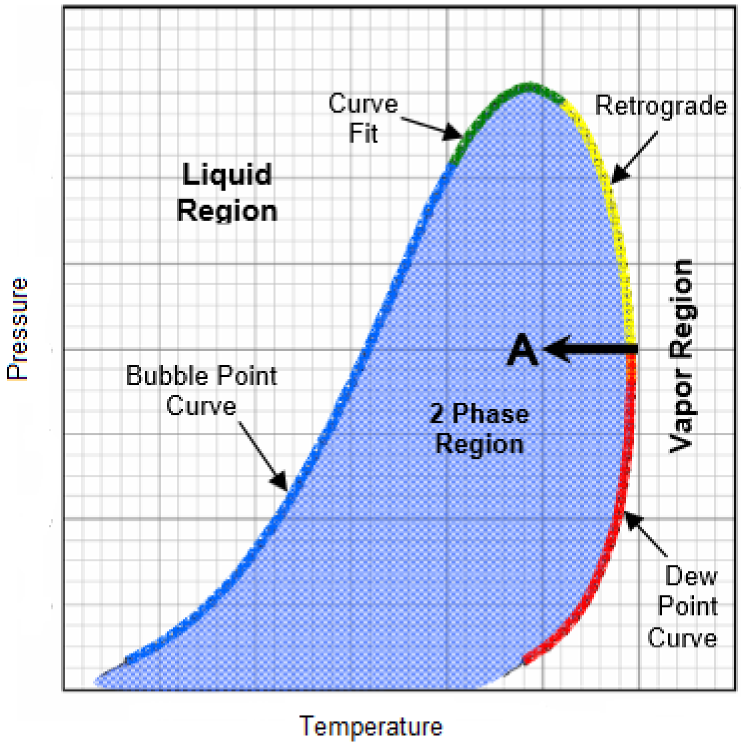

Figure 1.7: Example of natural gas phase diagram **[1.14]**

The zone of retrograde condensation is a zone where a liquid phase appears if the pressure is decreased at a certain temperature.

The form of the phase envelope depends on gas compositions. More there are heavier hydrocarbons, larger is the curve.

Solubility in water has to be considered. This information helps for separation of the different components, but also for the production of the reservoir. In general, natural gases are slightly soluble in water. And water salinity decreases their solubility in water **[1.8]**.

1.2.2. Natural Gas Transportation

Pipeline network transports natural gas from the wellhead to the customer (Figure 1.8).

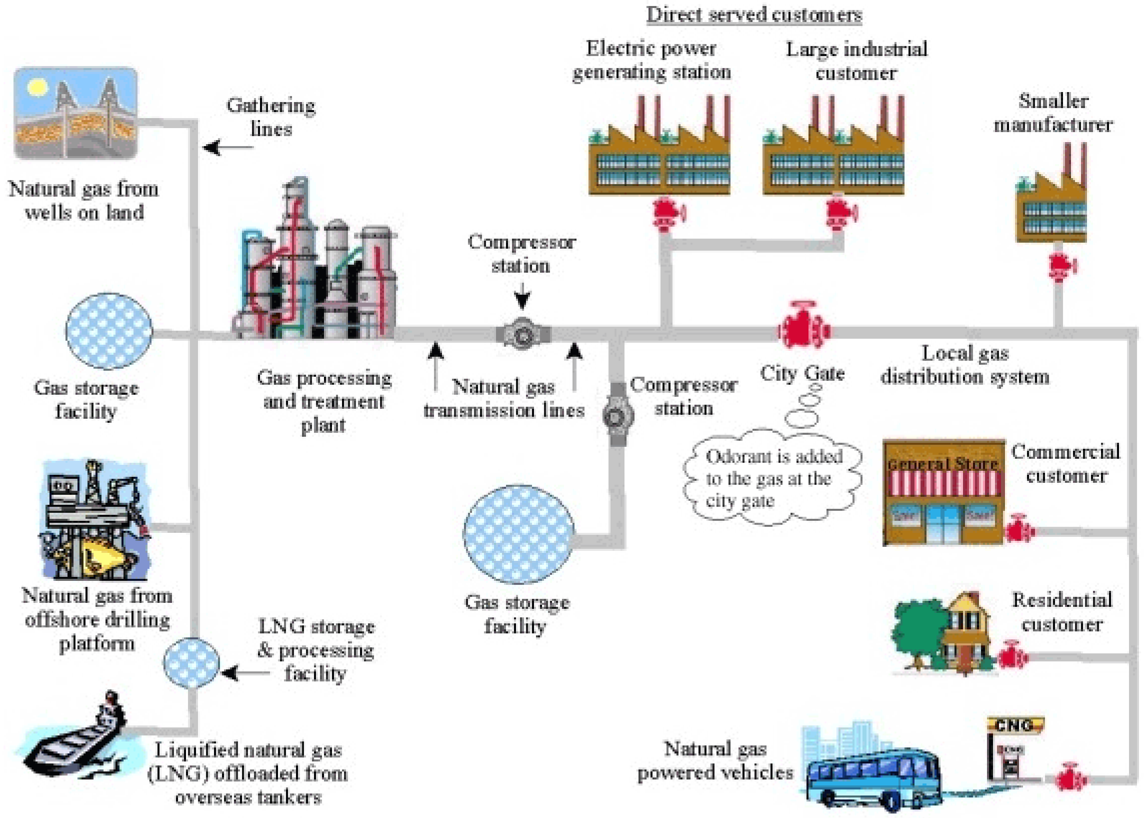

Figure 1.8: Natural gas pipeline network **[1.15]**

After drilling, natural gas is transported first to gas processing plants through flow lines and gathering lines (their specific features are explained in 1.2.2.1 and 1.2.2.2), then transmission systems to market areas and finally distribution lines to customers. There are mainly two transmission systems:

- Long-distance pipelines or mainline transmission systems;
- Gas carriers after methane liquefaction;

This work is focused on pipeline transport, which will be described below.

1.2.2.1. Flow Lines and Gathering Lines

Flow lines are connected to a single wellhead, while gathering lines collect gas from multiple flow lines. They transport raw gas to processing plants, where water and impurities are removed. Corrosive content is present in raw gas and may affect pipelines integrity. According to the U.S. Environmental Protection Agency (EPA), “Methane leakage from flow lines is a significant source of emissions in the gas industry” **[1.16]**. To prevent corrosion pipelines are protected with a special coating: a fusion bonded epoxy (resin).

Flow lines are narrow pipelines (with diameter as small as 0.5”) and the operating pressure is about 1.7 MPa, while gathering pipelines are larger, with a diameter under 18”, made of steel and carrying compressed gas at 4.9 MPa **[1.17]**.

Since the gas has not been treated, heavier hydrocarbons (from propane) may condense during the transport and form a liquid phase. The transport becomes multiphase.

1.2.2.2. Transmission and Distribution Lines

Transmission and distribution lines transport treated gas to customers. Transmission lines are usually long-distance and large pipelines (from 10” to 42” in diameter) made of steel, while distribution lines are categorized as regional systems **[1.17]**. They are also covered of a protective coating, but corrosion and material failure may happen. Indeed, even if the gas is considered as dry gas, there is still a certain amount of water, which may condense at a certain point, and acid gases. Some filters, used as liquid separators may be installed with the compression stations to purify as much as possible the gas before its compression.

Gas is carried at pressure from 1.4 to 8.3 MPa, usually in single phase **[1.17]**. For safety reason, the gas is compressed (Figure 1.9) and then transported and delivered under dense phase.

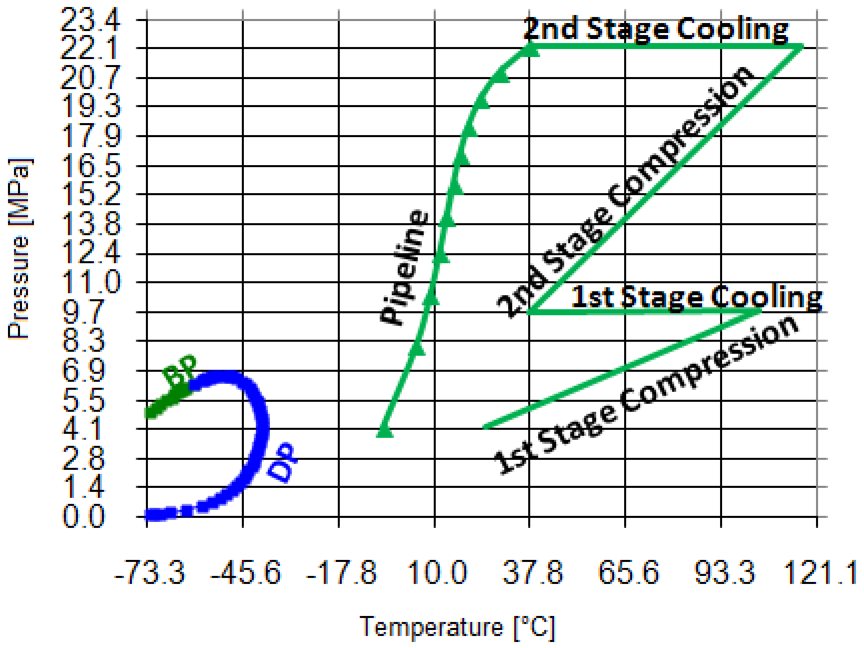

Figure 1.9: Natural gas phase envelope and compression conditions **[1.18]**

To ensure that the flow remains pressurized, compression stations are placed at 64 to 1600 km along the pipeline **[1.19]** (Figure 1.10).

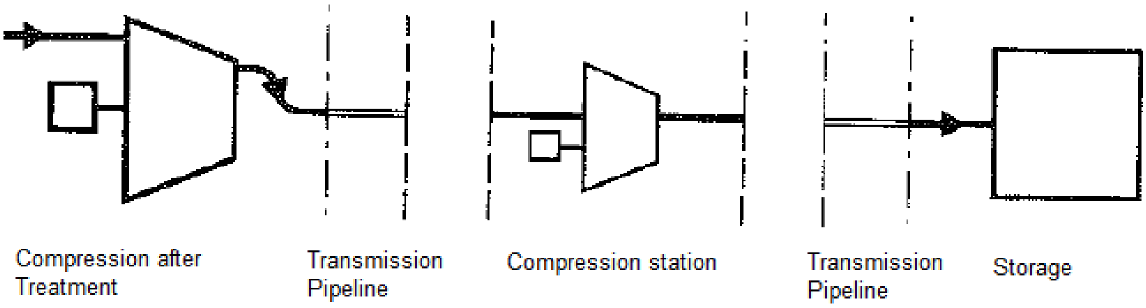

Figure 1.10: Transport chain **[1.8]**.

It is compressed by a turbine, operating thanks to the combustion of a proportion of the gas carried, or by an electric motor, requiring a reliable source of electricity around **[1.15]**.

Compared to methane liquefaction and transport by gas carrier, pipeline transport is the simplest and cheapest solution **[1.8]**.

1.3. CARBON DIOXIDE TRANSPORT

1.3.1. Sources of Carbon Dioxide

Emissions of greenhouse gases (methane, carbone dioxide, ozone, nitrous oxide...) are associated to a global world warming. It is expected to increase to 6.4 K by the end of the 21st century **[1.20]**. Several and serious consequences may be related to global warming: rising of sea level, more frequent natural disasters (hurricane, flood etc), rainfall disruption, changes in agriculture yields, disappearance of certain species and increase of disease-carrying insects.

Carbon dioxide is the largest contributor. It is mainly released by the combustion of fossil fuels and the burning of forests (Figure 1.11).

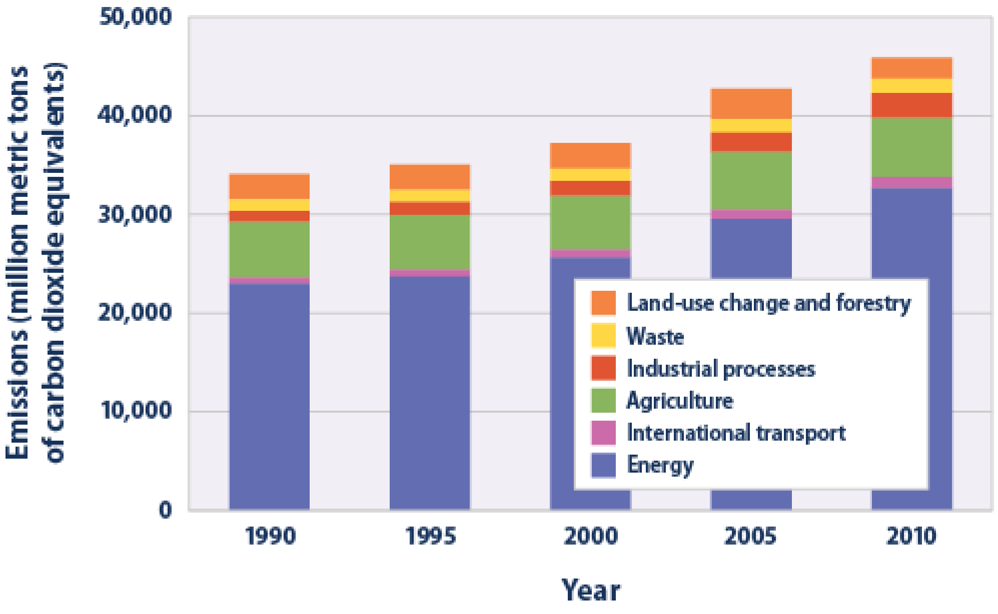

Figure 1.11: Global carbon dioxide emissions by sector between 1990 and 2010 **[1.21]**.

Carbon dioxide emissions from combustion of fossil fuels are estimated at 30 gigatons per year. Petroleum represents the majority of CO_2 emissions (approximately 43 %) among all fossil fuels. They may come from both stationary (e.g. power plants) and non-stationary (e.g. conveyance) **[1.9]**. For example, natural gas combustion is used in power plants to produce electricity and carbon dioxide and water produced are currently vented to the atmosphere.

1.3.2. Carbon Dioxide Capture

A promising solution to reduce carbon dioxide emissions to the atmosphere is Carbon dioxide Capture and Storage (CCS). It is captured from power plants, transported and stored in suitable geological storage for a long-term. Three capture ways are possible (Figure 1.12):

- Post-combustion capture
- Oxy-combustion capture
- Pre-combustion capture

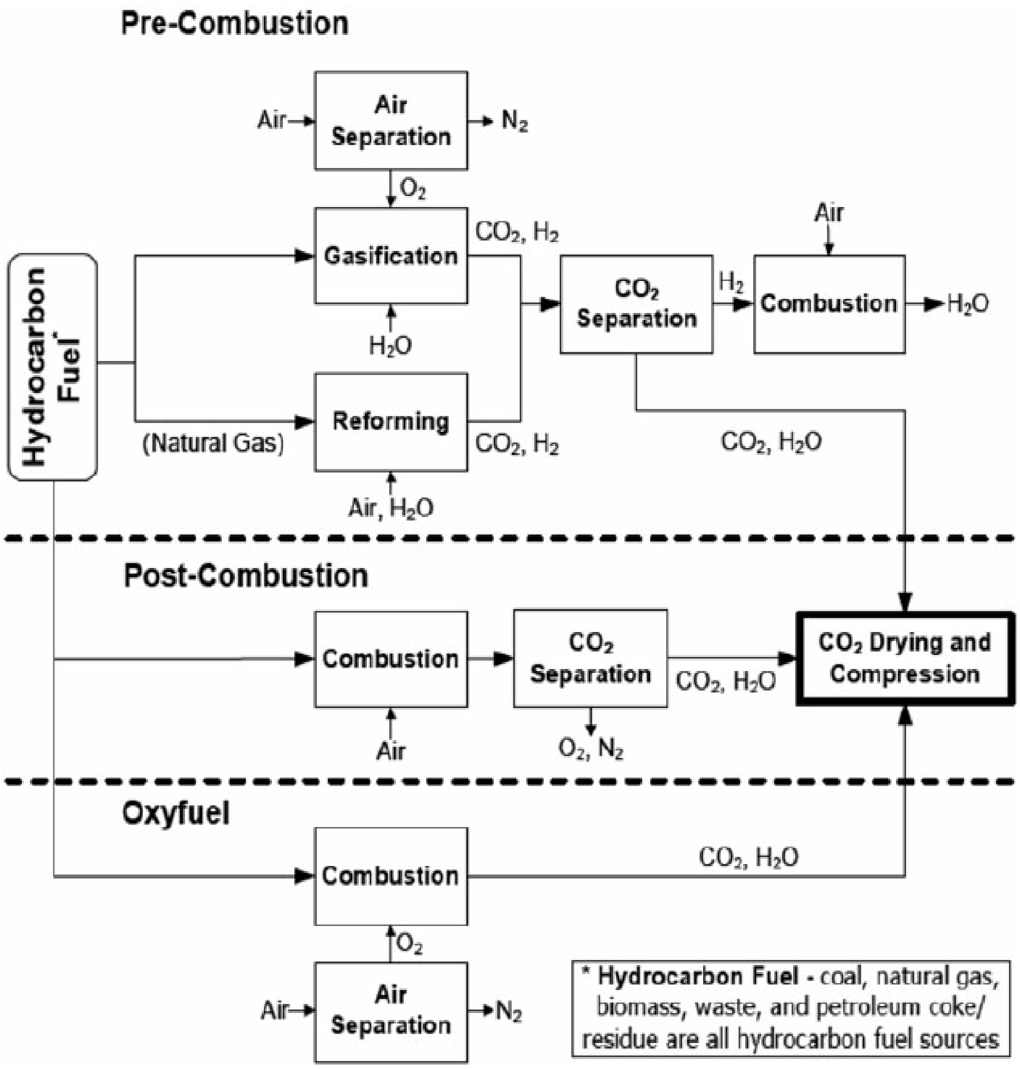

Figure 1.12: Schematic of processes for carbon dioxide capture **[1.9]**.

In the case of CCS, carbon dioxide captured is not pure. Impurities concentration varies depending on capture technology used. These impurities, H_2O, N_2, O_2, Ar, CH_4, SO_2

and H_2S, and SO_x and NO_x in the case of post-combustion capture, have to be considered in thermodynamic studies.

1.3.2.1. Post-Combustion Capture

Fossil fuels are combusted in the presence of air. Flue gases are produced and a solution would be to compress and inject them into geological storage or reuse in Enhanced Oil Recovery (EOR). But more energy would be needed for the compression and there would be more constraints to be considered on geological storage. Therefore, carbon dioxide is extracted from the flue gases produced. But its concentration is relatively low (its partial pressure is generally between 0.1 and 0.2 bar) considering the huge quantities of nitrogen (air) used for the combustion. It is a downstream process: carbon dioxide is removed by a chemical absorption process using alkanolamines at near atmospheric pressure. About 90% of CO_2 is recovered **[1.22]** and will be transported to storage reservoirs. The rest of the flue gas, a majority of nitrogen with carbon dioxide, water and oxygen is released to the atmosphere. An example of flue gas features is given in Table 1.2.

Table 1.2: Example of properties of flue gases from thermal power plants **[1.22]**

	Units	**Natural Gas**	**Coal**
Capacity	MWe	600	600
Flue gas flow rate	Nm^3/h	3 300 000	1 700 000
Density	kg/Nm^3	1.3	1.3
Temperature	°C	95-105	85-120
Pressure	MPa	0.1	0.1
Composition			
CO_2	%vol	3.5	13.5
H_2O	%vol	7	7-11
N_2	%vol	75-80	70-75
O_2	%vol	13.5	4
H_2	%vol	-	-
CO	%vol	-	10-25
Ar	%vol	0.02	0.9

Table 1.2 (to be continued): Example of properties of flue gases from thermal power plants **[1.22]**

	Units	**Natural Gas**	**Coal**
Composition			
NO_x	mg/Nm^3	25-50	200
SO_x	mg/Nm^3	0-35	150-200
HCl	ppm	-	4
NH_3	ppm	-	<1
Ashes	mg/Nm^3	<5	30
Heavy metals (Hg, Mn, Ni, Pb…)	µg/Nm^3	-	<5 (each)

1.3.2.2. Oxy-Combustion Capture

Oxy-combustion is combustion in the presence of pure oxygen. It increases the concentration of carbon dioxide in flue gases. These gases are mostly carbon dioxide and water. Therefore, capture process is reduced to water condensation. But the major obstacle is the necessity to have a continuous oxygen flow, with purity greater than 95% to limit nitrogen content, which presents a high cost. The temperature of combustion has also to be taken into account: it is increased from 1 900 °C with air (21% of oxygen) to 2 800 °C with 95% of oxygen. It can be an advantage, with the possibility to intensify heat transfers. But a solution to reduce the temperature would be to re-inject the carbon dioxide recovered. Other advantages are:

- Decrease of emissions and of flue gases flow rate (decrease of costs of flue gases treatment, smaller equipments, etc)
- Better efficiency (decrease of fuel consumption)

Although this technique is already applied in some industries (glass, cement, metals…), it is still at the state of research for an oxy-combustion in boilers.

1.3.2.3. Pre-Combustion Capture

The aim of pre-combustion is to form carbon dioxide before the combustion step. The fuel is converted to a syngas (a mixture of carbon monoxide and hydrogen). The steam reaction is the suitable process for natural gas (R-1.2):

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

(R-1.2)

It is an endothermic reaction that is why hydrogen production is done in furnaces. Before the oven, the temperature is between 540 and 580 °C. To move out the vapour from the catalyst, the temperature in the oven is between 850 and 900 °C. Pressure is between 2 and 3 MPa **[1.22]**.

The syngas is treated through a *shift conversion* to increase hydrogen production (R-1.3).

$$CO + H_2O \rightarrow CO_2 + H_2$$

(R-1.3)

This reaction is done in two furnaces:

- The principal reactor is a High Temperature Shift: it operates between 400 and 415 °C
- A smaller reactor, a Low Temperature Shift, increases the conversion of carbon monoxide. It operates from 220 to 240 °C.

Carbon dioxide is formed during this reaction and can be captured while hydrogen is burned to produce energy. Since CO_2 partial pressure is greater than the one for post-combustion, it is possible to extract carbon dioxide by physical solvent, like methanol. There are still research efforts to simplify the entire process scheme and to reduce costs **[1.22]**.

1.3.3. Carbon dioxide Transportation

Carbon dioxide can be either used for Enhanced Oil Recovery (EOR) or stored in underground geological reservoirs or used in chemical processes. Regardless of its destination, it is compressed for transport. Typical pipeline conditions are between 10 and 15 MPa, at pressures above its critical point (7.4 MPa), to avoid multiphase flow, increase the density and reduce the volume to be transported. Temperature is equivalent to the surrounding temperature: it varies seasonally and depends on regions, from below zero to 279.15-281.15 K, with peaks at 293.15 K in tropical regions.

There are three compression devices used to enable transport in single phase **[1.9]**:

- Compressors, which move gas at differential pressures (from 0.2 to 450 MPa);
- Blowers, which move large volumes of gas up to 0.3 MPa;
- Fans, which move gas up to 0.015 MPa.

Ship conditions are 0.7 MPa and 223.15 K **[1.9]** (Figure 1.13).

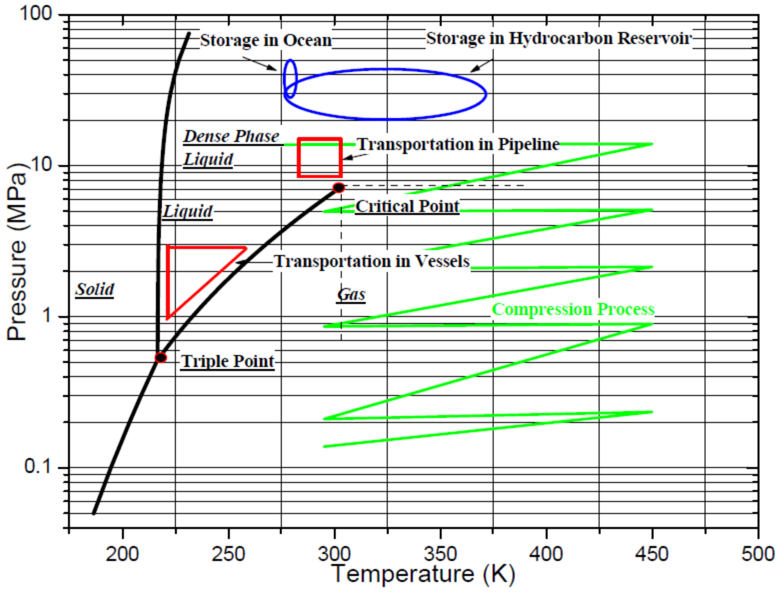

Figure 1.13: Temperature and pressure conditions of the CCS systems **[1.20]**

Design of pipeline diameter depends on different parameters: pressure drop, elevation change, carbon dioxide mass flow rate, compressibility and viscosity. But these properties are highly influenced by impurities. Indeed, a two-phase region appears as the purity of carbon dioxide decreases (Figure 1.14).

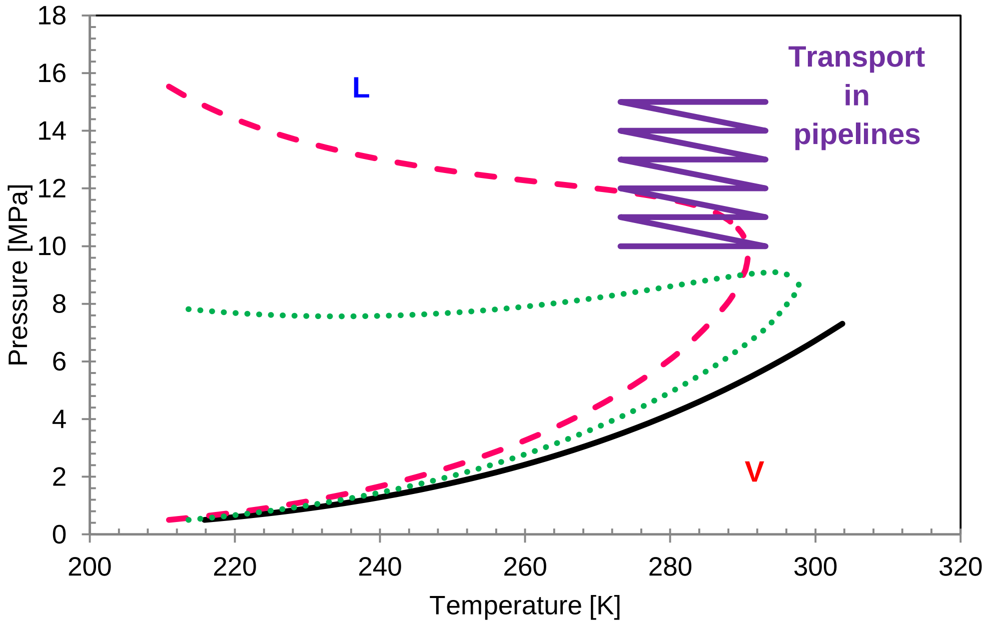

Figure 1.14: Phase diagram for different $CO_2 - N_2$ mixtures (▬▬) $99.99\%_{mol}$ CO_2+$0.01\%_{mol}$ N_2. (⋯⋯) $90\%_{mol}$ CO_2+$10\%_{mol}$ N_2. (▬ ▬) $80\%_{mol}$ CO_2+$20\%_{mol}$ N_2.

Moreover, for the same temperature and pressure, fluid density may be up to 35% less **[1.23]**, which has a serious impact on transportation: the energy needed for compression is increased or transport happens at lower densities.

Therefore, accurate phase diagrams and representation of density and viscosity of pure CO_2 and CO_2 mixtures are necessary for an efficient design of pipelines and a safe transport.

1.4. PROBLEMS ENCOUNTERED

As seen in part 1.2 and 1.3, natural gas and carbon dioxide are transported in the presence of various impurities. The major one in both cases is water, which is also one of the major wastes in the oil and gas industry. Presence of water and acid gases in pipeline may lead to corrosion (pipeline rupture) and hydrate formation (reason of pipeline blockage. These two phenomena are serious flow assurance issues.

1.4.1. Produced Water

Natural gas or oil produced are usually saturated with *formation water* **[1.24]**. In addition to formation water, there are two other sources of produced water:

- *Injected water*: to produce in the right conditions, the pressure must be maintained in oil reservoirs. Water with additives is injected in parallel wellbores and recovered later with the produced oil.
- *Condensed water*: water is also present in the gas phase in the reservoir. During the drilling and the transport, temperature and pressure conditions may change and water can condense. It is thus recovered as liquid phase.

These three sources of water are called produced water. It is the major waste in oil and gas industries. It is estimated at 250 million barrels per day compared to 80 million barrels of oil per day, which is equivalent to water cut of 70% **[1.25]**. Different factors may affect the amount of produced water, like the location of the well or the method of drilling. But the water rate is inherent to the well considered. On the other hand, mechanical problems may be the cause of unexpected increases of water production. Excessive pressure, material failures or holes caused by corrosion can let unwanted reservoir fluids enter the casing. Pump failure may also cause casing leaks. They occur usually above the top of the cement, so the drilling mud enters the wellbore.

Composition of produced water includes different sort of compounds **[1.25]**:

- *Dissolved and dispersed oil compounds*: BTEX (Benzene, Toluene, Ethylbenzene and Xylenes) are the most soluble compounds in produced water. They cannot be removed efficiently by oil/water techniques.
- *Dissolved gases*: carbon dioxide, nitrogen, oxygen and hydrogen sulphide are the most common gases in produced water.
- *Dissolved formation minerals*: cations and anions which affect water salinity. Salinity is mainly due to dissolved sodium and chloride. Salt concentration may vary from few ppm to 300 g/L. There are also traces of heavy metals such as mercury, copper, silver and zinc and Naturally Occurring Radioactive Materials (NORM).
- *Production chemical compounds*: additives in injected water, like treatment chemicals (corrosion inhibitors, biocides, antifoam...). Their concentration is lower than 0.1 ppm, except for corrosion and scale inhibitors, which can have a serious environmental impact **[1.26]**.
- *Solids*, like corrosion products, bacteria, waxes and asphaltenes.

In gas fields, there is no necessity to inject water. Therefore produced water is only a mixture of formation water and condensed water, so its volume is less than in oil fields.

Produced reservoir fluids are generally in equilibrium with the *formation water* and therefore contain significant quantities of water. In parallel, carbon dioxide is captured and transported with some amounts of water. In both cases, water content may lead to several problems. Corrosion is the first one. It can weaken pipelines. Because temperature and pressure conditions can change during the transport, it may lead to water condensation and to hydrate formation.

1.4.2. Corrosion

Presence of water and acid gases in natural gas transportation may lead to corrosion of pipelines. Corrosion is commonly defined as an irreversible deterioration of a material because of a chemical reaction with its environment. It induces to a degradation of the material. If the reaction continues with the same intensity, the metal can be completely converted into metal salts. High content of chromium and nickel prevents the corrosion of the alloy. But these types of steels are not used for pipelines, because it would be uneconomical. High-strength carbon steels (X65-X80) are generally used for pipelines **[1.27]**. A typical composition of additional compounds to iron is given in Table 1.3.

Table 1.3: Composition of the mild carbon steel X65 **[1.28]**.

X65	**C**	**Si**	**Mn**	**S**	**P**	**Cr**	**Ni**	**V**	**Mo**	**Cu**	**Al**	**Sn**
$\%_{wt}$	0.057	0.22	1.56	0.002	0.013	0.05	0.04	0.04	0.02	0.01	0.041	0.001

Dissolved carbon dioxide is the most prevalent form of corrosion: it promotes electrochemical reaction between steel and the aqueous phase. Because the formed carbonate Fe CO_3 has a low solubility in water, a corrosion layer grows on pipeline surface. In addition, the presence of hydrogen sulphide may also cause corrosion and pipeline failures (Sulphide Stress Corrosion Cracking).

Corrosion rate is dependent on the partial pressure of carbon dioxide **[1.29]**. 25% of failures in oil and gas industry are due to corrosion **[1.29]**.

1.4.3. Gas Hydrates

Discovered in 1810 by Sir Humphrey Davy, gas hydrates became source of interest for the hydrocarbon industry in 1934 **[1.30]**, due to the blockage of pipelines.

1.4.3.1. What are Gas Hydrates?

Gas hydrates are solid crystalline compounds, formed through a combination of water (host molecules) and small molecules (guest molecules under vapour or liquid state) under low temperature and elevated pressure conditions (e.g. 3-10 MPa and 275-285 K for methane hydrate **[1.31]**), stable above the ice point of water.

In general, considering a mixture of non polar (e.g. hydrocarbons) and polar molecules (e.g. water), there is no strong interactions between the solute and the solvent. Therefore, each molecule of solute is trapped into a cage of solvent. This cage involves hydrogen bonds. The solute is stabilised in the cage thanks to hydrophobic interactions **[1.32]**.

More precisely, water molecules can be described as having two positive and two negative charges. The hydrogen bond, as proposed by Latimer and Rodebush **[1.33]** in

1920, is the attraction of the positive pole of a water molecule to the negative pole of another molecule (Figure 1.15).

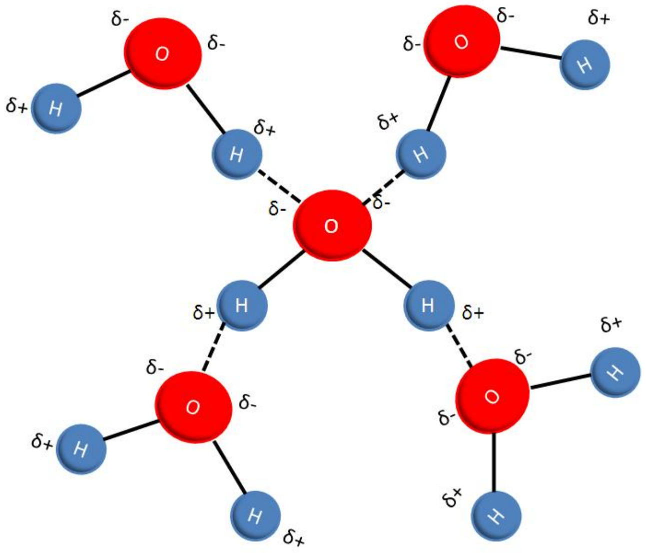

Figure 1.15: Hydrogen bonding between five molecules of water.

In this way, a water molecule is attached to four others, forming a network whose cavities are filled by guest molecules (e.g. CH_4 or CO_2).

The most common gas hydrates structures are structure I (sI) and structure II (sII) **[1.34]**. The existence of a third structure (sH) was discovered in 1987 by Ripmeester et al. **[1.35]**. Guest molecules in structure I are small molecules with a diameter between 4.2 and 6 Å[3] (e.g. methane, carbon dioxide and hydrogen sulphide). Structure II guest molecules are larger molecules, with diameters between 6 and 7 Å (e.g. propane, isobutane). Larger molecules (up to 9 Å) accompanied with small molecules (typically the one forming sI) can form structure H (cycloheptane, methylcyclohexane, 2,2-dimethylbutane). Besides common hydrate formers, some hydrocarbons have unusual behaviours. For example, cyclopropane is either a sI or sII hydrate former, entering in the larger cages of these two types. As for *n*-butane, it is a transition component. It is not a hydrate former itself, but can enter in the large cages in structure II in the presence of smaller hydrate former. Alkanes smaller than *n*-butane are hydrate former, while the one wider do not form hydrates. Hydrogen is a particular case. For a long time, it has been considered as non-hydrate former, based on the assumption that it was too small to stabilize cavities. But it has been shown that it can form structure II hydrates at very high pressures (200 MPa at 280 K) or cryogenic temperatures (145 K) **[1.36, 1.37]**.

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[3] Ångstrom: 1 Å is equal to 0.1 nm

SI and sII hydrates are cubic structures, formed by two types of water cages, while sH is a hexagonal structure with three different types of water molecules (Figure 1.16).

Other hydrate structures have been reported: the tetragonal structure of bromine hydrate **[1.38]** and the trigonal structure of dimethyl ether hydrate **[1.39]**.

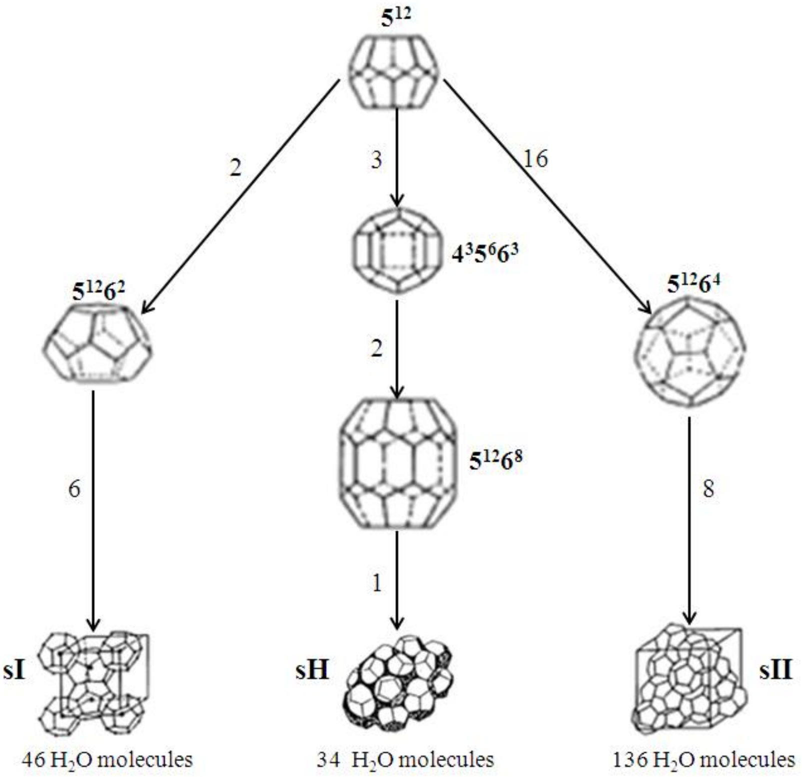
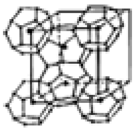
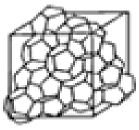
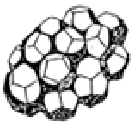
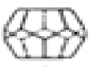
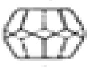
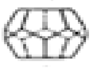
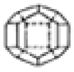
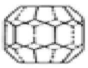


Figure 1.16: Hydrates structures **[1.40]**

Table 1.4 gives a brief description of the geometry of the different cages.

These structures are non-stoichiometric hydrates, since not all cages are filled. The occupancy depends on system pressure and temperature, and on the nature of the guest molecules. For example, about 96% of the cages are occupied in methane hydrates **[1.31]**.

Table 1.4: Geometry of cages in the three hydrates structures [1.40]

	Structure I		**Structure II**		**Structure H**		
Cavity							
	Small	**Large**	**Small**	**Large**	**Small**	**Medium**	**Large**
Description	5^{12} 	$5^{12}6^{2}$ 	5^{12} 	$5^{12}6^{4}$ 	5^{12} 	$4^{3}5^{6}6^{3}$ 	$5^{12}6^{8}$ 
Number of cavities/unit cell	2	6	16	8	3	2	1
Average cavity radius [a] **(Å)**	3.95	4.33	3.91	4.73	3.91[b]	4.06[b]	5.71[b]
Variation on radius[c] **(%)**	3.4	14.4	5.5	1.73	Not available		
Coordination number[d]	20	24	20	28	20	20	36
Number of waters/unit cell	46	136	34				

[a] *The average cavity radius varies with temperature, pressure and guest composition.*

[b] *Estimates of structure H cavities from geometric models.*

[c] *Variation in distance of oxygen atoms from centre of cage.*

[d] *Number of oxygen atoms at the periphery of each cavity.*

1.4.3.2. Hydrates Occurrence

Three conditions are necessary to form hydrates: suitable temperature and pressure conditions (usually low temperatures and high pressures), suitable sized molecules and the presence of water.

In natural gas or carbon dioxide processing and transportation, hydrate formation are a consequence of unusual flow line operations, and can block pipelines in the worst scenario (Figure 1.17).

Figure 1.17: Gas hydrates removed from a pipeline **[1.41]**

It occurs principally in gathering pipelines, before gas drying and during transient operations such as restarts after emergency shut-ins. The fluid arrives to process facilities at low temperature and it may not be completely dehydrated, so hydrate formation can also happen in transportation pipeline or after a restriction (choke or valve). Moreover, as the oil and gas industry moves into deeper water, the risk of hydrate formation in long subsea tiebacks is increasing.

Hydrate formation is similar to a crystallization process. There are two principle stages:

- *Hydrate nucleation or induction time*: temperature and pressure conditions are the one of hydrate stability zone, but no hydrate is forming. It is a metastable state, where a non equilibrium state lasts for a long time. The memory effect has an effect on induction time. If hydrates were formed and dissociated or if water was under ice form, the induction time is reduced;
- *Hydrate growth*: rapid hydrate formation and growth with the consumption of the gas present.

As for hydrate dissociation, it is an endothermic process: by supplying heat, hydrogen bonds forming the cages can be broken.

From a kinetic point of view, hydrate formation may be very long and difficult considering the induction time. Compared to formation process, hydrate dissociation is quite easier. Unlike hydrate thermodynamics, the kinetic of formation is difficult to be measured and modelled **[1.34]**.

Methane hydrates are also naturally present in the ocean at depths greater than 500 m and permafrost (Figure 1.18).

Figure 1.18: Known and expected methane hydrates locations in the World **[1.42]**.

They are considered today as a considerable potential source of energy, since the reserves are estimated to be between 2.10^3 and 4.10^6gigatons **[1.43]**. But conventional reservoirs can be present in the same locations and drilling operations through hydrates can be very hazardous. Indeed, drilling through hydrate bearing sediments may change the temperature and the pressure of the sediments and then destabilize the hydrates. It may lead to wellbore instability with an enlargement of the wellbore and even a collapse or changes of mechanical and physical properties of the sediments **[1.44]**. Hydrates may form again when dissolved gas rises to the surface, forming plugs in subsurface equipments (around the drill string in the riser, the casing and the blowout preventer). Whether in pipelines or during the drilling, plugs may cause equipment damage but also injury and even life loss. But, removing hydrates plug is time-consuming, expensive and can be dangerous depending on the location. Therefore to drill and transport the gas safely, it is important to understand hydrates formation conditions and to prevent them.

1.4.3.3. Thermodynamic Inhibitors

Several techniques have been developed to avoid hydrates formation. The first ones are based on hydrate formation conditions. Since it is necessary to have water to form hydrates, a solution would be to dehydrate the gas before its transport. It is usually done during on-shore processing, but it is, for the moment, difficult to apply for deepwater production. Another way is to reduce the pressure below the hydrate formation pressure. If the pipeline is already plugged, pressure must be reduced equally on both sides of the blockage to avoid the movement at high velocity of the plug along the line **[1.45]**. A more frequent method is to heat up the system, but again it is harder to apply on deepwater facilities. Chemical inhibition is the widely used technique to prevent hydrate formation, either in on-shore or off-shore production. Methanol and ethylene glycol are particularly used in the natural gas industry, but also ethanol to a lesser extent **[1.34]**. By reducing water activity, they allow a decrease of the temperature and an increase of pressure: the hydrate phase boundary is shifted enough to be able to operate outside hydrates stability zone.

Methanol is less expensive than glycols and therefore has been prevalent in the industry. But, because of its volatility, high concentrations are required, usually from 25 to 50% by volume in produced water **[1.46]**. Considering these high concentrations, some important issues have to be considered:

- Methanol is toxic**[1.47]**;
- The permitted total organic carbon levels in the wastewater are often exceeded due to methanol **[1.48]**;
- Due to its high vapour pressure, there are losses in the vapour phase. It therefore difficult and expensive to recover **[1.49]**.
- If methanol content is too high in oil or gas, refineries often impose penalties. For example, the penalty for methanol can be higher than 5$ per bbl (oil barrel) **[1.34]**.
- Spaces are limited for methanol storage on offshore platforms. It presents also a safety issue, since methanol is a flammable and easily ignited liquid, which flame is not visible when burning **[1.47]**;
- Methanol may concentrate in the liquefied petroleum gas (mostly propane with butanes). Nevertheless, propane and n-butane form azeotropes with methanol. So binary distillation is impossible to separate them **[1.45]**.

- Methanol may dissolve corrosion inhibitors, leading to corrosion problems in pipelines **[1.45]**.

The advantage of glycols is their low volatility, thus there are fewer losses in the vapour phase and it is easier to recover. Since they are usually used at low temperatures there are fewer losses. But they are also toxic. Their high viscosity leads to flow difficulties so they would be more efficient for plug removals **[1.49]**. From an economical point of view, glycols are more expensive than methanol. For years, inhibitors recovering has not been done, but for ecological reasons, it has to be considered now in the gas production plants and in financial plans **[1.45]**.

Another kind of inhibitors is developed, called kinetic inhibitors. Usually polymers, they are based on kinetic and not on thermodynamic equilibrium. They slow down hydrate formation and growth, so the fluids are transported without plug.

But thermodynamic inhibitors are still the most used in the industry, so it is important to improve and optimize their use. Accurate models and experimental data are essential for better understanding of the systems, safe production and transport. This work aimed to develop a predictive model allowing good predictions of phase equilibria, including hydrate stability zone. Measurements have been carried out to analyze complex systems, closest to the industrial ones, and validate the model.

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CHAPTER 2 – EXPERIMENTAL STUDY

Les diagrammes de phase sont utiles pour la conception et/ou l'optimisation de procédés. Ces diagrammes sont prédits à l'aide de modèles thermodynamiques. Pour être le plus précis possible, les paramètres de ces modèles sont ajustés sur des données expérimentales. Au cours de ce travail, des données d'équilibres liquide-vapeur et liquide-liquide ont été répertoriées et utilisées pour ajuster les paramètres de groupes de l'équation d'état GC-PR-CPA pour des systèmes binaires comportant de l'eau et/ou des alcools. D'autre part, des mesures expérimentales ont été effectuées dans le cadre de projets industriels. Il s'agit de compléter les bases de données sur des fluides réels, de mieux comprendre leur comportement ainsi que l'influence des impuretés et de valider les modèles. Ainsi, des mesures de points de bulle, d'équilibres liquide-liquide et principalement de points de dissociation d'hydrates ont été réalisées.

2.1. INTRODUCTION

Thermodynamic models are used to determine phase diagrams useful for process design and/or optimization. To develop these models and to adjust their parameters, it is necessary to have reliable experimental data. In the first part of this chapter, a literature review has been conducted. Vapour-Liquid Equilibrium (VLE) data have been gathered from the literature for binary systems with water and alcohols up to *n*-decane. These data have been screened and used to adjust the GC-PR-CPA EoS parameters C_{kl}, D_{kl} and E_{kl} (see *Chapter 4*). Then, experimental works have been performed to determine principally hydrate dissociation points but also VLE data and bubble points of multi-components systems. These measurements were carried out within the framework of several industrial projects. All of them consider the impact of acid gases on flow assurance but in different contexts: natural gas transport, carbon dioxide (from CCS) transport and acid gas injection.

Producing deepwater reservoirs, which involve low temperatures combined with high pressures and longer transfer times, means that the oil and gas industries has to deal with gas hydrate problems in subsea pipelines. With about 40% of untapped fields with high concentrations of CO_2 or H_2S **[2.1]**, it is important to have reliable data for such systems. But the existing data are limited especially for the real systems containing acid gases. These data are necessary to improve or validate the models, to improve predictions essential for strong design of production facilities. Therefore hydrate dissociation points have been measured for three multi-components systems in the presence of thermodynamic inhibitors (methanol, ethanol and ethylene glycol). Binary systems of methane with hydrogen sulphide without inhibitors have also been studied.

Furthermore, the presence of acid gases in natural gas is undesirable and they are stripped from the hydrocarbon stream. Nowadays, the principal technique to remove acid gases from natural gas processing plants is chemical absorption with amines. It has been shown **[2.2]** that these amines absorb also aromatic compounds. These aromatic compounds become therefore impurities in the acid gases stream and could have an impact on the acid gas compression process. They can potentially condense at high pressures in a sour liquid phase and can also impact hydrate formation conditions in the presence of water. VLE and hydrate dissociation points have been measured for different concentrations of acid gases in presence of aromatic compounds.

Carbon dioxide captured from power plants contains impurities (water, nitrogen, oxygen, hydrogen, methane, nitrous oxide...), which may lead to flow assurance issues and increasing processing cost. The presence of water may cause pipeline blockage with hydrate formation or pipeline rupture due to corrosion. Moreover, since carbon dioxide is compressed, the presence of impurities may change the physical properties of the stream (e.g. bubble point and viscosity) and therefore the conditions of compression and transport. The aim of the project is to investigate the phase behaviour of carbon dioxide in the presence of impurities. The effect of impurities has rarely been investigated and limited data are available for CO_2-rich mixtures. Status of VLE data available for binary systems of interest is presented in Table 2.1).

Table 2.1: VLE status of the bibliographic study. CD: Confidential Data. CR: Chemical Reaction. CRYO: Cryogenic measurements. DWA: Data Widely Available. ✓: one to ten references available in the literature. ND: No Data.

	CO_2	CO	N_2	O_2	Ar	H_2	NO	CH_4	C_2H_6	C_3H_8	NO_2	SO_2	H_2S	N_2O
CO_2		✓	✓	✓	✓	✓	✓	✓	✓	✓	CD	✓	✓	✓
CO			✓+ CD	CR	✓	✓	ND	✓	✓	✓	ND	ND	✓	ND
N_2				✓	✓	✓	✓	✓	DWA	ND	✓	✓	✓	
O_2					✓	ND	ND	CRYO	CD	✓	ND	✓	ND	✓
Ar						CRYO	ND	CRYO	✓	ND	ND	To be published	ND	ND
H_2							ND	✓	✓	✓	ND	ND	ND	ND
NO								✓	ND	ND	✓	ND	ND	ND
CH_4									DWA	ND	✓	✓		✓
C_2H_6										DWA	ND	ND	✓	✓
C_3H_8											ND	✓	✓	ND
NO_2												CR	ND	ND
SO_2													ND	ND
H_2S														ND
N_2O														

Among all systems investigated in this project, two have been studied by myself: a binary system carbon dioxide with argon and a CO_2-rich system. Bubble points and hydrate dissociation points have been measured.

2.2. REVIEW OF AVAILABLE EXPERIMENTAL DATA

Vapour-Liquid Equilibrium (VLE) and Liquid-Liquid Equilibrium (LLE) data are used to adjust the group parameters of the GC-PR-CPA EoS. An extensive literature review has been conducted to collect experimental data for binary systems with water and alcohols.

2.2.1. Binary Systems Containing Water

The solubilities of hydrocarbons, acid gases and inert gases (e.g. nitrogen and hydrogen) in pure water have been measured by many researchers. Some data are also available for water content. Several data have been found for light hydrocarbons. Data are more limited for heavier normal alkanes and branched alkanes as well as for naphthenic compounds except cyclohexane.

For a chosen system, all available data have been compared. Data which did not follow the major trend have been rejected (e.g. Figure 2.1).

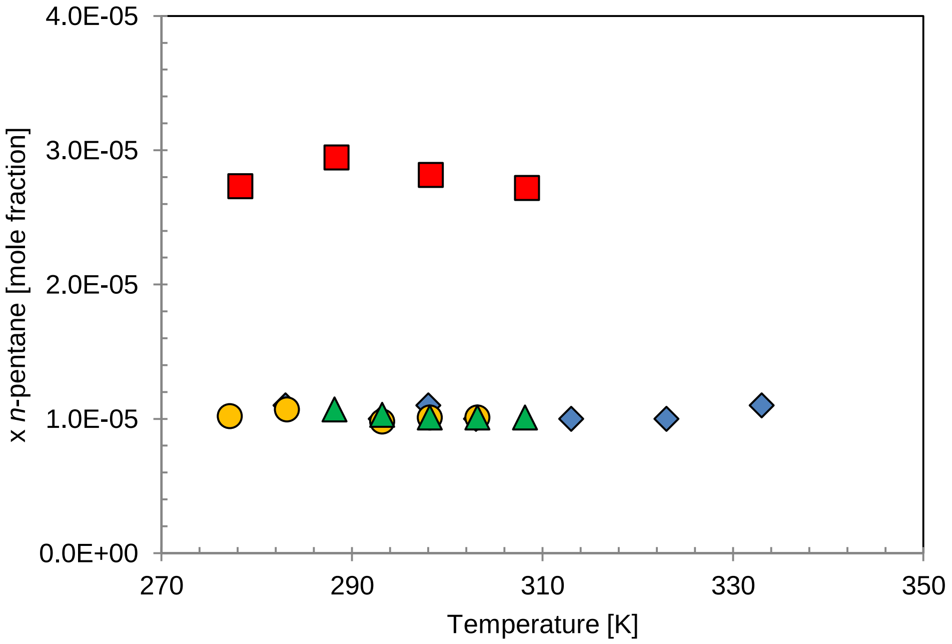

Figure 2.1: n-Pentane solubility in water at atmospheric pressure. Comparison of data from the literature (♦) **[2.3]**, *(▲)* **[2.4]**, *(●)* **[2.5]** *and (■)* **[2.6]**.

Sources of experimental data for binary systems with water are listed in Appendix A.1.

2.2.2. Binary Systems Containing Methanol

Methanol is one of the most commonly used hydrate inhibitor, especially during shut in and start-up. It is therefore important to have accurate knowledge of phase behaviour of systems containing methanol. VLE and LLE data of hydrocarbons, acid gases, inert gases and water with methanol are reported in Appendix A.2. Most of the data have been taken from the NIST (National Institute of Standards and Technology) database. The software ThermoData Engine from the NIST evaluates the accuracy of experimental data listed **[2.7-2.15]**. Some data have been therefore rejected after this evaluation.

2.2.3. Binary Systems Containing Ethanol

Ethanol is also used as a hydrate inhibitor in a lesser extent. It is commonly used in South America (e.g. Brazil). Compared to methanol, fewer data are available. The temperature and pressure ranges of studies are also more limited. Data collected are presented in Appendix A.3.

2.2.4. Binary Systems Containing Alcohols

Alcohols are used as solvents in extractive distillation for example. Since they form hydrogen bonds, it is also interesting to test the model for these compounds. Data gathered for *n*-propanol to *n*-decanol, *2*-propanol to *2*-octanol and *3*-pentanol are presented in Appendices A.4 to A.18.

2.3. EXPERIMENTAL EQUIPMENTS

2.3.1. Bubble Point

To validate the setup the binary mixture CO_2+Ar has been first studied. Then bubble points have been measured for a CO_2-rich mixture (MIX 1). The technique is based on a **synthetic method**

2.3.1.1. Apparatus

The apparatus used is a rocking cell, i.e. a piston-type variable volume (maximum volume of 300 cm^3), shown on Figure 2.2. The apparatus consists of an equilibrium cell, a cooling jacket, a rocking mechanism and pressure/temperature recording equipment controlled by a computer. The equilibrium cell is made of titanium and there is also a mixing ball inside. The cell volume (hence pressure) can be adjusted injected or removing liquid behind the moving piston. The rocking mechanism is a horizontal pivot associated to pneumatic controlled rocking through 180 degrees, at a rate of 8 times per minute.

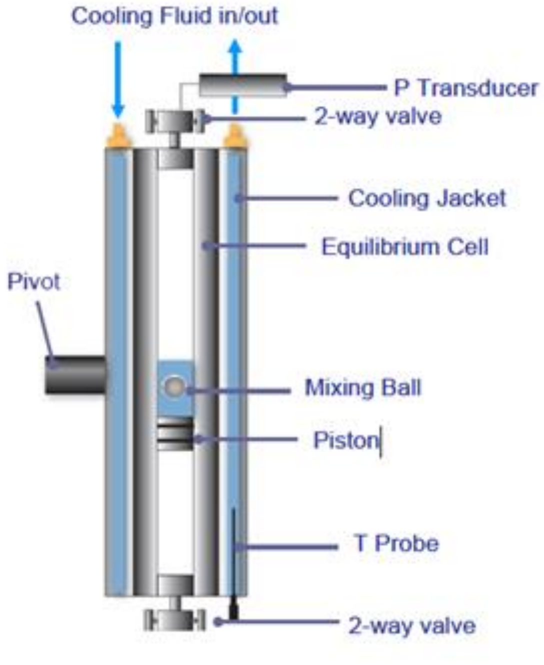

Figure 2.2: Schematic of apparatus used for bubble point measurements.

The working temperature range is from -80 to 80 °C, with a maximum operating pressure of 70 MPa. To ensure good temperature stability, the jacket is insulated with polystyrene and the connecting pipe covered with plastic foam. The temperature is measured with a Platinium Resistance Thermometer, located in the cooling jacket. The accuracy of temperature measurements is estimated to be ± 0.1 °C. The pressure is measured with a Quartzdyne pressure transducer, directly in the cell. The accuracy is estimated to be ± 8 kPa.

The mixture is prepared or directly loaded from a gas bottle in a piston vessel.

2.3.1.2. Materials

Since some measurements have been done for temperatures under the freezing point of water, a mixture of de-ionized water and ethylene glycol has been injected behind the moving piston of the equilibrium cell. De-ionized water has also been used to pressurize and maintain the pressure constant in the external piston vessel.

Carbon dioxide and argon used for the first experiment were 99.99 % pure and supplied by BOC (UK).

The composition of the CO_2-rich synthetic mixture (MIX 1) is given in Table 2.2.

Table 2.2: Composition of each component (mole %) of mixture MIX 1

Components	**MIX 1**
CO_2	94.92
CO	0.21
O_2	0.80
Ar	1.21
CH_4	0.63
H_2	0.82
N_2	1.41

2.3.2. Vapour-Liquid Equilibrium Data

Complete PTxy data have been measured for acid gases mixtures.

2.3.2.1. Apparatus

Figure 2.3 shows the apparatus used for VLE measurements. The equilibrium cell (EC) is totally immersed in a liquid bath regulated by a temperature controller. Techniques are based on a **static-analytic method**, thus both liquid and vapour phase are sampled with two capillary samplers. The composition of the samples is determined with a gas chromatograph (Perichrom model PR-2100) equipped with two thermal conductivity detectors (TCD and FID). Two platinium resistance probes are used to measure the temperature: one is located at the upper of the cell and the other one at the bottom. The accuracy of temperature measurements is estimated to be ±0.1 °C. A pressure transducer (range: 0-160 bar) measures the pressure in the cell. It is maintained at a constant temperature of 110 °C by a in-house air-thermostat, controlled by a PID regulator. The accuracy of pressure measurements is estimated to be ±8 kPa. Temperature and pressure probes are connected to a HP data acquisition unit.

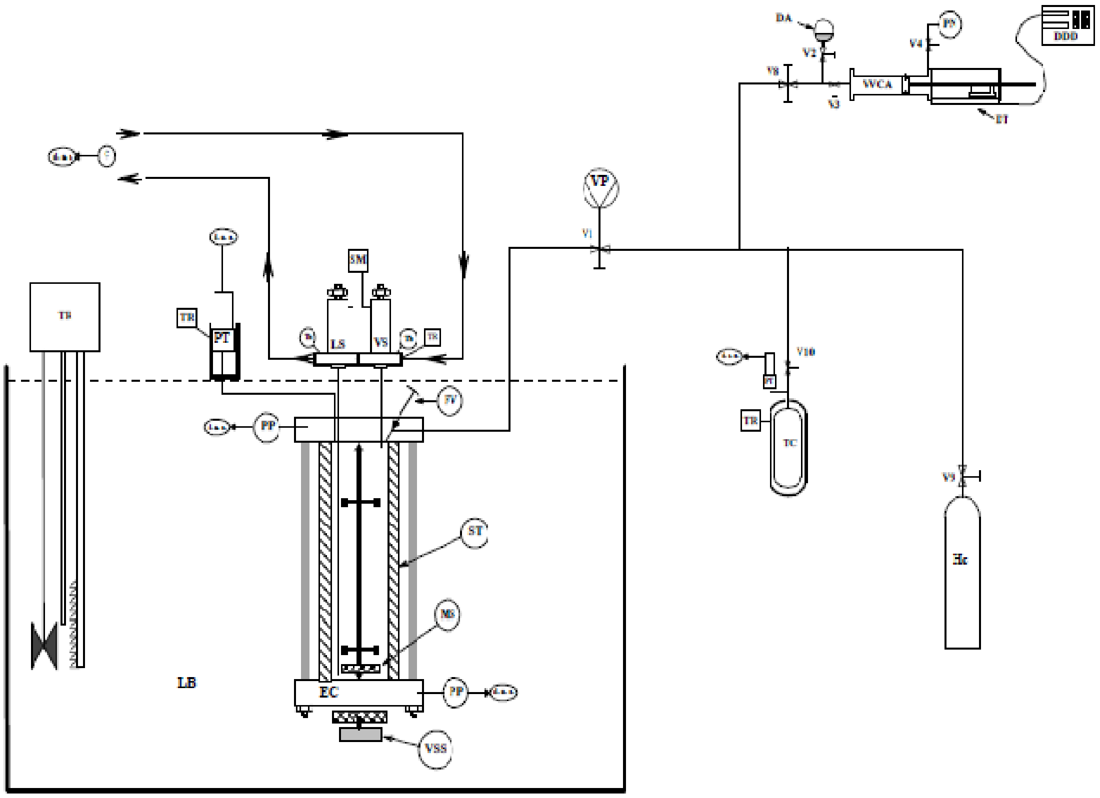

Figure 2.3: Flow diagram of the equipment used for VLE measurements. EC: equilibrium cell; PT: pressure transducer; LB: liquid bath; PP: platinum probe; SD: stirring device; TR: temperature regulator; VP: vacuum pump.

2.3.2.2. Materials

The project includes measurements with several compositions of acid gases (CO_2+H_2S).

Table 2.3: Materials used for VLE measurements

Components	Purity [%]	Suppliers
Carbon dioxide	99.995	Air Liquide
Hydrogen sulphide	99.5	Air Liquide
Light hydrocarbon mixture (methane, ethane and propane)	Ethane: 99.80 Propane: 99.90 Methane: balance	Air Liquide
Benzene	99.9	VWR

Table 2.3 (to be continued): Materials used for VLE measurements

Components	Purity [%]	Suppliers
Toluene	99.9	Sigma-Aldrich
***m*-Xylene**	99.0	Sigma-Aldrich
Cyclopentane	99	Sigma-Aldrich

In this work, VLE measurements have been done for one mixture (MIX 2). Its composition is given in Table 2.4.

Table 2.4: Composition of each component (mole %) of mixture MIX 2

Components	MIX 2
Hydrogen sulphide	51.20
Carbon dioxide	22.19
Methane	2.62
Ethane	0.31
Propane	0.15
Cyclopentane	0.71
Benzene	13.64
Toluene	7.53
m-Xylene	1.65

2.3.3. Hydrate Dissociation Point

Hydrate dissociation point measurements have been the bulk of the experimental work carried out during this thesis. The measurements have been conducted in the presence of thermodynamic inhibitors (methanol, ethanol and ethylene glycol). Measurements have also been done for CO_2-rich systems and acid gases. The technique is based on static synthetic method.

2.3.3.1. Apparatus

Two types of equilibrium cells have been used for hydrate dissociation point measurements: one in Heriot Watt University and the other one in Mines ParisTech.

The first one is a mixed autoclave rig, made of Hastelloy (Figure 2.4). The cell volume is about 125 mL. The cell is held in a cooling jacket or immersed directly in a temperature-controlled liquid bath. To achieve thermodynamic equilibrium and to mix well the fluids, a stirrer with a magnetic motor is used. A platinium resistance probe measures the temperature. The accuracy of temperature measurements is ±0.1 °C. A Quartzdyne pressure transducer is mounted directly on the cell. The accuracy of pressure measurements is about ±5 kPa. Both pressure and temperature monitors are connected to a computer for a direct acquisition.

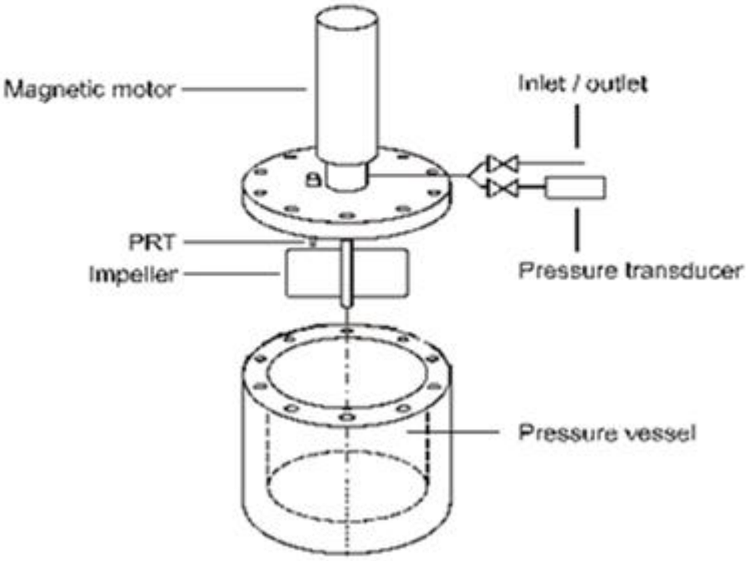

Figure 2.4: Schematic of apparatus used for hydrate dissociation point measurements.

The working temperature range is from -70 to 50 °C and up to 70 MPa.

Figure 2.5 shows the other equilibrium cell (EC). It is a cylindrical vessel with two sapphire windows. The cell is immersed in a temperature controlled bath (LB and TR). A stirring device (SD) is also used. The pressure is measured with one of the two pressure transducers (PT), for a pressure range up to 16 MPa (LPT) and 70 MPa (HPT), depending on the experimental pressure range. The pressure accuracy is less than 5 kPa. The temperature is measured with two platinium resistance thermometers (PP). The temperature accuracy is estimated to be less than 0.1 °C.

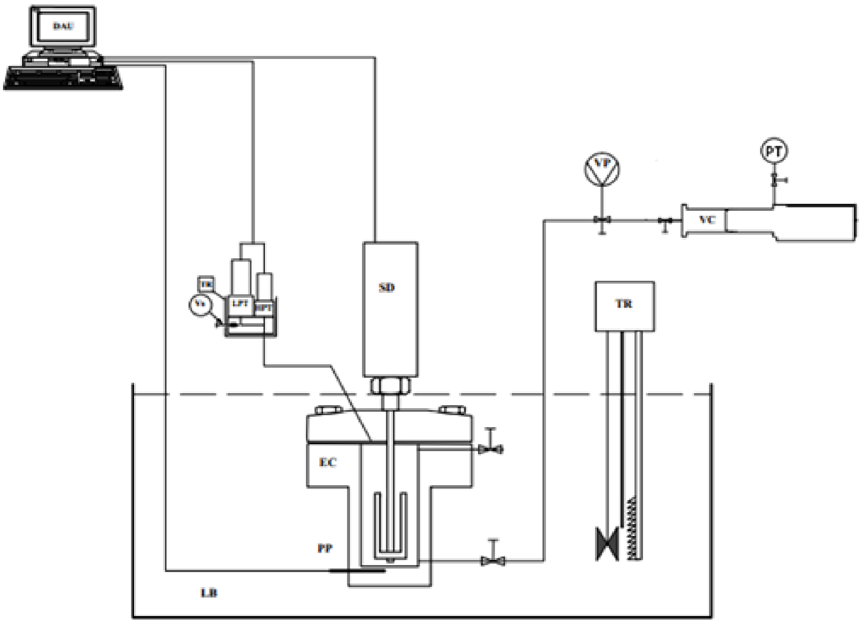

Figure 2.5: Schematic flow diagram of the apparatus. EC: equilibrium cell; PT: pressure transducer; LB: liquid bath; PP: platinum probe; SD: stirring device; TR: temperature regulator; VP: vacuum pump.

2.3.3.2. Materials

- **CO_2-rich mixtures**

For this project, the systems studied are the same ones as for bubble point measurements. The material used has been thus already presented in 2.2.1.2.

- **Acid gases mixtures**

The material used is the same as the one presented in 2.3.2.2. Two mixtures, MIX 3 (Table 2.5) and MIX 4 (Table 2.6) have been studied.

Table 2.5: Composition of each component (mole %) of mixture MIX 3

Components	MIX 3
Hydrogen sulphide	22.03
Carbon dioxide	50.61
Methane	1.66
Ethane	0.19

Table 2.5 (to be continued): Composition of each component (mole %) of mixture MIX 3

Components	MIX 3
Propane	0.10
Cyclopentane	0.76
Benzene	14.73
Toluene	8.13
m-Xylene	1.79

Table 2.6: Composition of each component (mole %) of mixture MIX 4

Components	MIX 4
Hydrogen sulphide	40.29
Carbon dioxide	41.70
Methane	1.18
Ethane	0.14
Propane	0.07
Cyclopentane	0.52
Benzene	9.62
Toluene	5.32
m-Xylene	1.16

- **Natural gas with acid gases mixtures**

De-ionized water has been used in all tests. Thermodynamic inhibitors have also been used: methanol, ethanol and ethylene glycol (MEG) were all 99+% pure.

Four mixtures have been studied. The two first one are based on a natural gas supplied by BOC. CO_2 (99.995% pure) has been added by weight ($10\%_{wt}$ and $25\%_{wt}$). The compositions of these two gas mixtures (MIX 5 and MIX 6) are given in Tables 2.7 and

2.8. For a same mixture, several samples have been prepared to measure enough points for all systems of interest.

Table 2.7: Composition of each component (mole %) of mixture MIX 5

Components	**MIX 5-1**	**MIX 5-2**	**MIX 5-3**	**MIX 5-4**
Nitrogen	6.33	6.36	6.36	6.36
Methane	76.11	76.48	76.49	76.48
Ethane	4.22	4.25	4.25	4.25
Propane	2.12	2.12	2.12	2.12
***n*-Butane**	0.84	0.85	0.85	0.85
***n*-Pentane**	0.84	0.85	0.85	0.85
Carbon dioxide	9.54	9.09	9.08	9.09

Table 2.8: Composition of each component (mole %) of mixture MIX 6

Components	**MIX 6**
Nitrogen	5.60
Methane	67.31
Ethane	3.74
Propane	1.87
***n*-Butane**	0.74
***n*-Pentane**	0.74
Carbon dioxide	20.00

The third mixture (MIX 7) contains 70%$_{\text{mol}}$ of CO_2. It has been supplied by BOC and the composition is given in Table 2.9.

Table 2.9: Composition of each component (mole %) of mixture MIX 7

Components	**MIX 7**
Methane	20.00
Ethane	6.60
Propane	2.60
***i*-Butane**	0.40
***n*-Butane**	0.40
Carbon dioxide	70.00

Finally, since limited data are available for systems with hydrogen sulphide, hydrate dissociation points have been measured for the binary system 80%$_{mol}$ methane (99.995% purity) with 20%$_{mol}$ hydrogen sulphide (99.5% purity). Both gases were supplied by Air Liquide.

2.4. EXPERIMENTAL PROCEDURES

2.4.1. Calibration

During this thesis, the probes on apparatus used for hydrate dissociation point measurements have been calibrated again. Results are presented below.

2.4.1.1. Pressure Transducer Calibration

The pressure transducer used is calibrated using a dead weight balance: Desgranges and Huot, France, 5202 model. The uncertainty given by the manufacturer is 200 mbar. Experimental field is between 30 and 75 bars, so calibration has been done between 1 and 82 bar (Table 2.10).

Table 2.10: Pressure transducers calibration

Pressure transducer	**Field [bar]**	**Calibration Field [bar]**	**Accuracy [bar]**
PT 200	0-200	1-82	±0.01

Calculation of uncertainties of pressure measurements is given in Appendix B (Table B.2).

2.4.1.2. Platinium Probe Temperature Calibration

Both temperature probes used are calibrated on a very high precision standard platinium probe 25 Ω (Fluke Hart Scientific Model 5628). This standard probe is connected to an Ohmmeter Agilent 344420A and has been previously calibrated by the "Laboratoire National d'Essai" (LNE, Paris). The uncertainty given by the manufacturer is 0.013 °C. Calibration field corresponds to the temperature range of hydrate measurements (from -20 to 25 °C). Calibration results are presented in Table 2.11.

Table 2.11: Temperature probes calibration

Temperature probe	Calibration Field [°C]	Accuracy [°C]
Bottom	-20 – 40	±0.03
Upper	-20 – 40	±0.04

Calculation of the uncertainties of temperature measurements is given in Appendix B (Table B.1).

2.4.2. Constant Mass Expansion

Bubble points are measured through a **constant mass expansion study**. First the cell is cleaned and vacuumed. Then the mixture is loaded from an external piston vessel. The vessel is pressurized and kept above the bubble pressure. During the loading, distilled water is injected behind the moving piston to ensure that the mixture is loaded as a single liquid phase.

After the loading of the cell, water is injected behind its moving piston to reduce the sample volume and to increase the pressure significantly to be higher than the expected bubble point. For measurements at temperatures below the freezing point of water, a mixture water + alcohol or water + glycol is injected instead of distilled water. The temperature is set to and the cell is rocked to mix all components and to ensure equilibrium.

Then the sample volume is increased step by step by removing measured quantities of the pumped liquid behind the piston. At each step, the mixing is kept until reaching equilibrium, indicated by a constant pressure.

For each temperature, the stabilized equilibrium pressure is plotted as a function of the mass or volume of the different samples removed: the bubble point is indicated by slope change in the plot. It is the intersection between the two curves (see Figure 2.24).

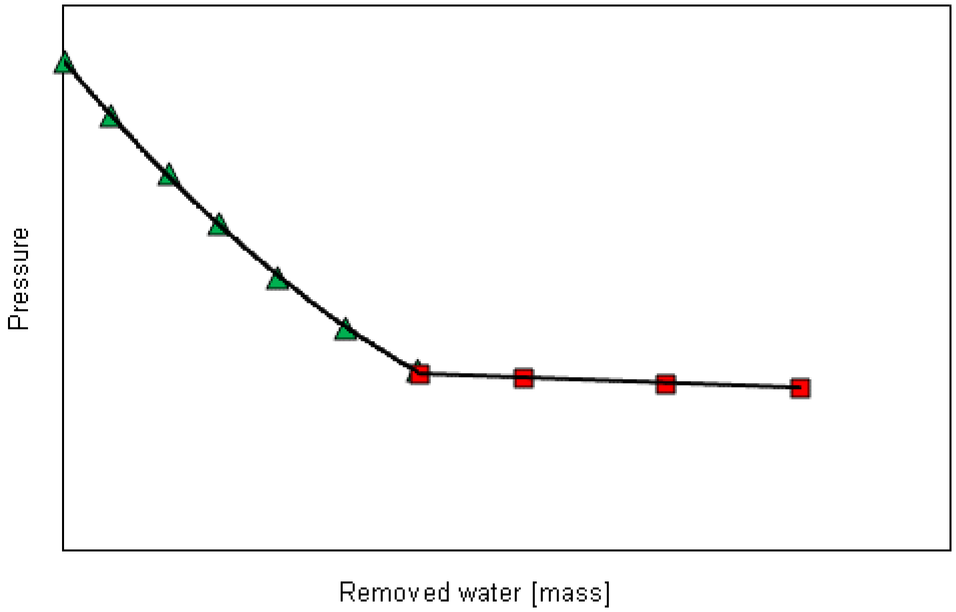

Figure 2.6: Pressure – mass diagram to determine the bubble point at constant temperature. ▲ *above the bubble point.* ■ *bubble line.*

2.4.3. Static-Analytic Method

First the equilibrium cell is cleaned and vacuumed while the mixture is prepared in an external piston vessel. The hydraulic side of the piston is pressurized with nitrogen up to 10 MPa. Then the mixture is loaded into the equilibrium cell in a single liquid phase, until the required pressure and temperature are reached. When a constant pressure and temperature are observed, the sampling and its analysis are conducted and repeated for both liquid and vapour phases. A gas chromatograph (*GC*) is used for the samples analysis. A RT-Qplot column is used to separate all compounds. Detectors have been previously calibrated for each compound. With this calibration, a relation between the surface given by the *GC* and the number of moles is established, allowing the determination of the mixture composition in both phases.

2.4.4. Isochoric Pressure Search Method

Hydrate dissociation points are measured using the **isochoric pressure search method**. The equilibrium cell is cleaned, vacuumed and charged with deionised water. It is then immersed into the bath. The binary mixture is prepared in a high-pressure cylinder and it is injected into the vessel (as a single supercritical phase), until the desired pressure, well above the hydrate stability zone. After achieving a thermodynamic equilibrium, the temperature is continuously decreased to form hydrates. Hydrate formation is detected with a pressure drop. Then the temperature is increased step by step and kept constant at each step to reach the temperature and pressure equilibrium. If the temperature is increased in the hydrate zone, the pressure increases significantly, but if the temperature is increased outside the hydrate zone, there is a small increase of pressure due to the thermal expansion. Consequently, the dissociation point is the intersection between the two slopes (Figure 2.7).

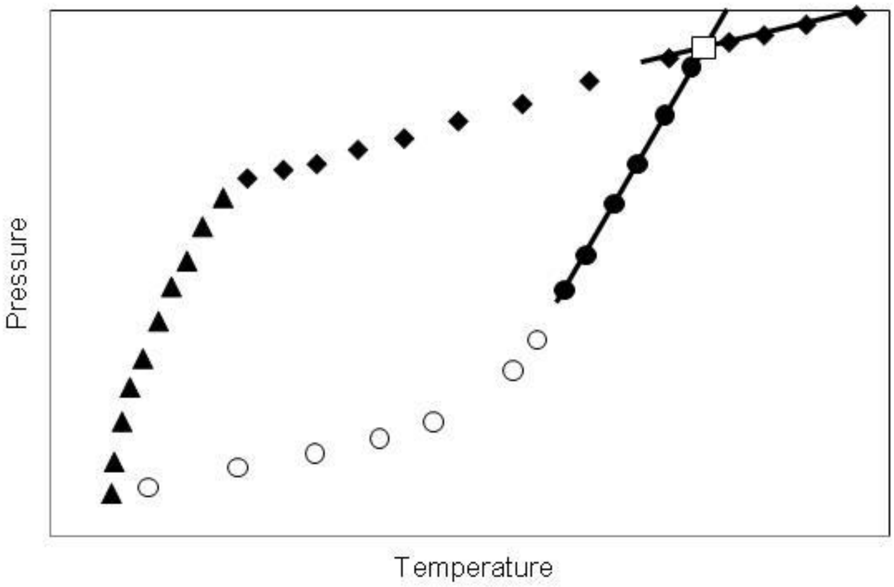

Figure 2.7: Pressure – temperature diagram for estimating hydrate dissociation point. ♦ thermal expansion, ▲ pressure drop (hydrate formation), ○ heating, ● step by step heating, □ hydrate dissociation point

2.5. EXPERIMENTAL RESULTS

2.5.1. Bubble Point Measurements

Bubble point measurements were carried out for the carbon dioxide – argon binary system and for the multicomponent mixture MIX 1 from -30 to 20 °C. The results are listed in Tables 2.12 and 2.13.

Table 2.12: Experimental bubble points of the 95% CO2 + 5% Ar binary system

Temperatures [K] (±0.1)	**Pressures [MPa] (±0.005)**
243.25	3.902
253.15	4.316
263.15	4.888
273.15	5.550
278.15	6.109
283.05	6.412
283.15	6.591
288.15	7.005
293.15	7.481

Table 2.13: Experimental bubble points of MIX 1 (Table 2.2)

Temperatures [K] **(±0.1)**	**Pressures [MPa]** **(±0.005)**
248.25	5.172
253.15	5.340
263.25	5.755
273.15	6.340
273.15	6.251
278.15	6.507
283.15	6.836
288.25	7.160
293.25	7.710
293.25	7.678

2.5.2. Vapour-Liquid Equilibrium Measurements

The experimental results of MIX 2 (Table 2.4) are given in Tables C.1 and C.2 in Appendix C.

2.5.3. Hydrate Dissociation Point Measurements

2.5.3.1. CO_2-Rich Mixtures

Experimental hydrate dissociation conditions of 95% CO_2 + 5% Ar are presented in Tables 2.14 and in 2.15 for MIX 1.

Table 2.14: Experimental hydrate dissociation conditions in the presence of distilled water of the system 95% CO_2 + 5% Ar (aqueous fraction between 0.92 and 0.85)

Temperatures [K] (±0.1)	**Pressures [MPa] (±0.005)**
277.2	2.089
280.1	2.976
281.0	3.578
282.0	4.093
283.1	4.785
284.3	7.864

Table 2.15: Experimental hydrate dissociation conditions in the presence of distilled water of MIX 1 (aqueous fraction between 0.92 and 0.85)

Temperatures [K] (±0.1)	**Pressures [MPa] (±0.005)**
274.3	1.522
276.7	1.987
278.4	2.421
279.5	2.840
280.5	3.200
281.5	3.682

2.5.3.2. Acid Gases mixture

Hydrate dissociation points for acid gases mixtures MIX 3 and MIX 4 are given in Appendix D (Tables D.1 and D.2). Uncertainties of measurements have been determined. Calculation procedures and results for hydrate dissociation conditions of MIX 3 are presented in Appendices E and F.

2.5.3.3. Natural Gas with Acid Gases Mixtures

Experimental hydrate dissociation conditions of MIX 5, MIX 6 and MIX 7 are presented in Tables 2.16, 2.17 and 2.18 in the presence of different aqueous solutions.

Table 2.16: Experimental hydrate dissociation conditions with gas mixtures MIX 5 (Table 2.7) in the presence of distilled water and different aqueous solutions

Aqueous phase compositions (±0.1)	**Gas mixtures**	**Aqueous Fractions (±0.001)**	**Temperatures [K] (±0.1)**	**Pressures [MPa] (±0.03)**
Deionised water	MIX 5-1	0.973	278.6	1.76
		0.949	284.4	3.47
		0.895	289.2	6.90
		0.771	292.9	13.90
	MIX 5-2	0.737	294.5	19.94
		0.699	296.0	26.59
25%$_{wt}$ ethanol	MIX 5-2	0.972	270.3	1.74
		0.941	276.2	3.52
		0.890	281.3	6.71
		0.770	284.7	13.37
	MIX 5-3	0.738	286.4	18.67
		0.671	288.5	28.13
25%$_{wt}$ methanol	MIX 5-4	0.977	267.7	1.84
		0.958	272.8	3.45
		0.917	277.2	6.6
		0.873	279.4	10.12
		0.828	280.5	13.83
		0.732	282.2	21.09

Table 2.16 (to be continued): Experimental hydrate dissociation conditions with gas mixtures MIX 5 (Table 2.7) in the presence of distilled water and different aqueous solutions

Aqueous phase compositions (±0.1)	**Gas mixtures**	**Aqueous Fractions (±0.001)**	**Temperatures [K] (±0.1)**	**Pressures [MPa] (±0.03)**
25%$_{wt}$ MEG	MIX 5-3	0.907	277.2	3.33
		0.828	281.5	6.49
	MIX 5-4	0.711	284.6	10.50
		0.681	285.5	13.22
		0.604	286.8	18.74
		0.541	287.6	20.18
		0.475	288.2	23.68
50%$_{wt}$ ethanol	MIX 5-4	0.950	268.6	4.14
		0.917	271.4	6.88
		0.881	273.4	9.91
		0.802	278.0	16.24
		0.780	278.2	18.79
50%$_{wt}$ methanol	MIX 5-4	0.922	259.4	4.92
		0.881	261.6	7.15
		0.823	262.8	11.14
		0.790	263.6	14.59
		0.753	264.3	18.48
50%$_{wt}$ MEG	MIX 5-4	0.874	267.9	6.98
		0.837	270.7	12.74
		0.780	271.3	16.71
		0.775	272.2	20.79
		0.750	273.6	23.89

Table 2.17: Experimental hydrate dissociation conditions with gas mixtures MIX 6 (Table 2.8) in the presence of different aqueous solutions

Aqueous phase compositions (±0.1)	**Aqueous Fractions (±0.001)**	**Temperatures [K] (±0.1)**	**Pressures [MPa] (±0.03)**
25%$_{wt}$ ethanol	0.966	267.0	1.64
	0.916	273.8	3.60
	0.863	278.6	6.73
	0.792	281.8	10.32
	0.729	283.0	13.92
	0.701	283.7	15.98
	0.683	284.2	17.83
	0.666	284.8	20.16
25%$_{wt}$ methanol	0.963	269.5	2.54
	0.918	276.0	6.25
	0.882	277.8	9.16
	0.818	278.8	13.58
	0.777	279.5	15.63
	0.738	280.0	18.21
	0.725	280.1	19.40
25%$_{wt}$ MEG	0.946	273.3	2.30
	0.859	281.2	7.25
	0.798	282.3	10.19
	0.763	283.5	12.29
	0.724	284.8	14.95
	0.618	285.7	20.27

Table 2.17(to be continued): Experimental hydrate dissociation conditions with gas mixtures MIX 6 (Table 2.8) in the presence of different aqueous solutions

Aqueous phase compositions (±0.1)	**Aqueous Fractions (±0.001)**	**Temperatures [K] (±0.1)**	**Pressures [MPa] (±0.03)**
50%$_{wt}$ ethanol	0.945	258.9	2.87
	0.905	260.3	3.90
	0.786	267.0	9.23
	0.712	268.4	13.30
	0.742	269.4	17.33
50%$_{wt}$ methanol	0.915	256.7	3.99
	0.874	261.4	8.43
	0.832	262.4	12.72
50%$_{wt}$ MEG	0.973	264.3	3.76
	0.945	268.4	7.70
	0.923	269.2	10.00
	0.896	269.8	13.48
	0.874	270.6	17.08

Table 2.18: Experimental hydrate dissociation conditions with gas mixtures MIX 7 (Table 2.9) in the presence of different aqueous solutions

Aqueous phase compositions (±0.1)	**Aqueous Fractions**	**Temperatures [K] (±0.1)**	**Pressures [MPa] (±0.03)**
25%$_{wt}$ ethanol	0.973	263.1	0.93
	0.941	275.0	3.19
	0.852	277.5	6.64
	0.784	278.1	7.93
	0.736	279.0	10.62
	0.713	280.1	15.23
	0.702	280.8	17.57
25%$_{wt}$ methanol	0.948	269.5	1.76
	0.886	275.2	4.48
	0.846	276.3	7.42
	0.741	275.9	11.42
	0.707	276.9	16.26
	0.722	278.4	19.70
25%$_{wt}$ MEG	0.963	265.6	0.98
	0.892	278.2	4.21
	0.877	278.5	7.24
	0.775	279.3	8.80
	0.684	280.3	12.30
	0.637	280.7	14.73
	0.621	281.41	18.03

Table 2.18 (to be continued): Experimental hydrate dissociation conditions with gas mixtures MIX 7 (Table 2.9) in the presence of different aqueous solutions

Aqueous phase compositions (±0.1)	**Aqueous Fractions**	**Temperatures [K] (±0.1)**	**Pressures [MPa] (±0.03)**
50%$_{wt}$ ethanol	0.938	262.6	1.93
	0.905	268.5	3.20
	0.810	269.4	3.85
	0.668	269.9	4.70
	0.526	271.5	7.72
	0.517	274.5	17.86
	0.537	278.9	39.73
50%$_{wt}$ methanol	0.959	253.0	1.72
	0.906	258.3	3.39
	0.750	257.0	5.64
	0.728	257.5	7.31
	0.713	258.6	11.46
	0.690	261.4	24.38
	0.742	267.7	62.40
50%$_{wt}$ MEG	0.940	259.5	2.12
	0.908	263.5	3.63
	0.760	263.7	5.79
	0.728	265.0	8.07
	0.709	266.3	13.27
	0.722	268.1	21.34
	0.711	269.3	29.51

Table 2.19 presents hydrate dissociation conditions for the system 80%$_{mol}$ CH_4 + 20%$_{mol}$ H_2S.

Table 2.19: Experimental hydrate dissociation conditions in the presence of distilled water of 80%$_{mol}$ CH_4 +20%$_{mol}$ H_2S system

Aqueous Fractions (±0.001)	**Temperature [K] (±0.1)**	**Pressure [MPa] (±0.03)**
0.977	275.0	1.02
0.964	282.3	1.89
0.937	289.0	3.56
0.906	293.4	5.52
0.877	296.1	7.37
0.818	297.7	9.43

2.6. CONCLUSION

PTx and PTxy data for binary systems have been taken from the literature and will be used in Chapter 4 to adjust the GC-PR-CPA EoS group parameters C_{kl}, D_{kl} and E_{kl} and validate the model for binary mixtures. Phase equilibria and hydrate dissociation point measurements have been conducted for three industrial projects to better understand the behaviour of real systems encountered. Some of these data will be used in Chapter 5 to evaluate the accuracy of the model for multi-component systems.

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CHAPTER 3 - THERMODYNAMIC MODELLING: FROM PHASE EQUILIBRIA TO EQUATIONS OF STATE

Le pétrole et le gaz naturel sont des systèmes complexes dans lesquels les hydrocarbures sont produits avec de l'eau et différentes impuretés, telles que le dioxyde de carbone ou le sulfure d'hydrogène. Il est donc nécessaire de connaitre le comportement de ces fluides pour concevoir et optimiser les procédés de production et de traitement. Les diagrammes de phases permettent d'établir une « cartographie » du système en déterminant, par exemple, les compositions pour une température et une pression données. Ce chapitre présente dans un premier temps les équilibres entre phases. L'équilibre thermodynamique est défini par une enthalpie libre (ou énergie de Gibbs) minimum à une certaine température et pression. C'est dans ce cas qu'interviennent les modèles thermodynamiques, dont les équations d'état. Des équations d'états sont présentées dans une deuxième partie : les équations cubiques sont les plus utilisées dans l'industrie. Ces équations nécessitent de nombreux ajustements de paramètres pour représenter précisément les fluides pétroliers, dont les mélanges aqueux. Les modèles ont évolué vers de meilleures représentations des composés associatifs (eau, alcools, glycols) en tenant compte des différentes interactions entre les molécules, comme les liaisons hydrogène. L'équation d'état Cubic-Plus-Association (CPA), qui réunit une équation d'état cubique au terme associatif de Wertheim, est adaptée aux systèmes contenant des composés associatifs. Un autre modèle d'intérêt est un modèle de contribution de groupe Predictive Peng-Robinson (PPR78), qui évalue de façon prédictive les coefficients d'interaction binaire et permet donc de prédire les diagrammes de phase pour des systèmes d'intérêt sans réajustement des paramètres sur des données expérimentales.

3.1. INTRODUCTION

As seen in Chapter 1, multiphase flows are challenging for the oil and gas engineering, having a serious impact on production and transport. Water and impurities (carbon dioxide, hydrogen sulphide, nitrogen, helium...) are usually co-produced with oil and gas. It is also the case in CCS, even if the concentration and the type of impurities are different. Multiphase flows during transport influence the design of pipelines. It complicates the systems and affects their reliability by altering the performance characteristics (e.g. the pressure drop that determines the system's power requirements). Presence of water and acid gases during the transport increases the probability of pipeline corrosion and hydrates formation. To secure the transport, inhibitors (methanol, ethanol, ethylene glycol) are injected, and recovered at the end of the process. This supplementary aspect has also to be taken into account. Therefore, accurate phase diagrams, by showing the equilibrium conditions of different phases, have a great importance in the industry, being useful for the design of pipelines and for separation facilities (e.g. distillation). These diagrams can be predicted using thermodynamic modelling.

Models developed are based on Equations of State (EoS). Cubic equations of state, such as the Soave-Redlich-Kwong (SRK) Equation of State **[3.1]** and the Peng-Robinson (PR) EoS **[3.2]**, are widely used in the industry for several years. Their drawback rests on an incorrect prediction of species forming hydrogen bonds, e.g. water and alcohols. Therefore, equations of state have been developed to describe more accurately their behaviour, taking into account hydrogen bonding. The Cubic-Plus-Association (CPA) EoS **[3.3]** is suitable for these systems. Another interesting model is the Predictive Peng-Robinson (PPR78) EoS **[3.4]**. It allows good predictions for natural gas systems (without water) by calculating a predictive temperature dependent binary interaction parameter. Both models are described in this chapter after a description of phase equilibria calculations.

3.2. PHASE EQUILIBRIA CALCULATIONS

3.2.1. Definition of Thermodynamic Equilibrium

For an isothermal and isobaric process, phase equilibrium is represented by Equation (3.1):

$$d_{T,P}G = 0 \tag{3.1}$$

Equation (3.1) is stable in the case of a single phase system and unstable in the case of a multiphase system.

The chemical potential μ is the macroscopic representation of the repulsive interactions of a molecule in a system and is related to the Gibbs free energy by:

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j,j\neq i}} \tag{3.2}$$

For an isothermal and isobaric process, one obtains Equation (3.3):

$$\sum_{i=1}^{c} \mu_i dN_i = 0 \tag{3.3}$$

To recap, phase equilibrium is characterized by:

- Uniformity of the temperature in the system (isothermal process):

$$T_i^{phase\ 1} = T_i^{phase\ 2}$$

- Uniformity of the pressure (isobaric process):

$$P_i^{phase\ 1} = P_i^{phase\ 2}$$

- Uniformity of chemical potentials:

$$\mu_i^{phase\ 1} = \mu_i^{phase\ 2}$$

For a component *i* considered as an ideal gas at a temperature *T*, the chemical potential is defined by:

$$\left(\frac{\partial \mu_i^{id}}{\partial P}\right)_T = v_i^{id} = \frac{RT}{P} \tag{3.4}$$

By integrating Equation (3.4) between two pressures, one obtains:

$$\mu_i^{id}(T,P) = \mu_i^{id}(T,P_0) + RT ln\frac{P}{P_0} \tag{3.5}$$

For the same component i in any phase, the chemical potential is defined as:

$$\mu_i^{phase\,1}(T,P,x^{phase\,1}) = \mu_i^{id}(T,P_0) + RTln\frac{f_i^{phase\,1}(T,P,x^{phase\,1})}{P_0}$$

(3.6)

where x is the composition of the component i in one phase and f is the fugacity. The fugacity depends on temperature, pressure and composition of the mixture. The fugacity is equivalent to a pressure and it represents the deviation to ideality.

Equation (3.7) is a generalised version of Equation (3.6):

$$\mu_i^{phase\,1}(T,P,x^{phase\,1}) = \mu_i^{standard} + RTln\frac{f_i^{phase\,1}(T,P,x^{phase\,1})}{f_i^{standard}}$$

(3.7)

The equilibrium defined by Equation (3.3) can also be applied to fugacities:

$$f_i^{phase\,1}(T,P,x^{phase\,1}) = f_i^{phase\,2}(T,P,x^{phase\,2})$$

(3.8)

3.2.2. Vapour – Liquid Equilibrium

The vapour – liquid equilibrium is defined by the equality of fugacities at given temperature and pressure.

The equality of fugacities is expressed as follows:

$$f_i^{Liq}(T,P,x_i) = f_i^{Vap}(T,P,y_i)$$

(3.9)

Where

- *Liq*: liquid phase
- *Vap*: vapour phase
- x: composition of the component i in the liquid phase
- y: composition of the component i the vapour phase

Fugacities can be calculated through two methods: the gamma – phi and the phi – phi method **[3.5]**.

3.2.2.1. The Gamma – Phi Approach

The gamma – phi approach uses a cubic equation of state for the vapour phase and activity coefficient model for the liquid fugacity.

- **Calculation of the fugacity in the vapour phase**

In the vapour phase, the fugacity is defined as follows:

$$f_i^{vap}(T,P,y_i) = \phi_i^{vap}(T,P,y_i).y_i.P$$

(3.10)

Where

- $\phi_i^{vap}(T,P,y_i)$ is the fugacity coefficient
- y_i is the composition of the component i in the vapour phase.

The fugacity coefficient is defined in the same way as for the phi – phi method (*see 3.2.2.2*).

- **Calculation of the fugacity in the liquid phase**

The fugacity in the liquid phase for the component i is defined by Equation (3.11).

$$f_i^{Liq}(T,P,x_i) = \gamma_i^{Liq}(T,P,x_i).x_i.f_i^{Liq,id}(T,P)$$

(3.11)

Where

- $\gamma_i^{Liq}(T,P,x_i)$ is the activity coefficient of the component i in the liquid phase
- $f_i^{Liq,id}(T,P)$ is the fugacity of the ideal liquid

The activity coefficient γ_i is related to the excess Gibbs energy.

$$ln(\gamma_i) = \frac{g_i^E(T,P,x_i)}{RT}$$

(3.12)

By defining the excess Gibbs energy, it is possible to define the activity coefficient. Several models exist to define the excess Gibbs energy. For example, Renon and Prausnitz **[3.6]** defined the NRTL (Non-Random Two-Liquid) model. It is based on the hypothesis of Wilson: the local concentration around a molecule *i* is different from the bulk concentration. This difference is due to the difference between the interaction energy of the central molecule i with the other molecules (same kind *i* and different kind *j*).

3.2.2.2. The Phi – Phi Approach

The phi – phi approach uses a cubic equation of state for both vapour and liquid phases. Then the equilibrium is given under the following form:

$$x_i\phi_i^{Liq}(T,P,x_i) = y_i\phi_i^{Vap}(T,P,y_i)$$

(3.13)

where φ_i is the fugacity coefficient. It is defined by Equation (3.14).

$$\phi_i(T,P) = \frac{f_i(T,P)}{P_i} \tag{3.14}$$

The fugacity coefficient can also be defined as a function of the residual Gibbs energy:

$$ln(\phi_i) = \left(\frac{\partial G_i^R}{\partial n_i}\right)_{T,P,n_{j\neq i}} \tag{3.15}$$

The residual Gibbs energy can be determined with an equation of state. The general expression for the residual Gibbs energy is given by Equation (3.16):

$$\frac{G^R}{RT} = Z - 1 - lnZ + \frac{1}{RT}\int_{\infty}^{V}\left(\frac{RT}{V} - P\right)dV \tag{3.16}$$

The compressibility factor Z is defined as follows:

$$Z = \frac{PV}{RT} \tag{3.17}$$

And P is defined by equation of states.

3.2.3. Cubic Equations of State

Besides the well known Van der Waals equation of state, its modified versions, the Soave – Redlich – Kwong (SRK) **[3.1]** and the Peng-Robinson (PR) **[3.2]** are the most commonly used in the industry (see Table 3.1).

Table 3.1: Classical cubic equations of state

Equations of state	Abbreviations	Expressions
Van der Waals	VdW	$P = \frac{RT}{v - b_i^{VdW}} - \frac{a_i^{VdW}(T)}{v}$
Soave-Redlich-Kwong	SRK	$P = \frac{RT}{v - b_i^{SRK}} - \frac{a_i^{SRK}(T)}{v\left(v + b_i^{SRK}\right)}$
Peng-Robinson	PR	$P = \frac{RT}{v - b_i^{PR}} - \frac{a_i^{PR}(T)}{v\left(v + b_i^{PR}\right) + b_i^{PR}\left(v - b_i^{PR}\right)}$

Parameters used in cubic equations of state are presented in Table 3.2.

Table 3.2: Parameters used in the cubic equations of state.

Parameters	Names	Values	Units
P	Pressure	System parameter	Pa
T	Temperature	System parameter	K
R	Ideal gas constant	8.314472	J.mol^{-1}.K^{-1}
v	Molar volume	System parameter	m^3.mol^{-1}
b$_i$	Co-volume of the component i	See (3.20)	m^3.mol^{-1}
a$_i$	Attractive parameter of the component i	See (3.18)	J.m^3.mol^{-2}

Calculations of the energy parameter and the co-volume are developed below.

- **Pure compounds**
    - Calculation of the attractive parameter

The attractive parameter for inert compounds is an adjustable constant for the VdW EoS, but it is temperature dependent in the SRK and PR EoS.

$$a_i(T) = a_{c,i}\underbrace{\left[1+\kappa_i\left(1-\sqrt{\frac{T}{T_{C,i}}}\right)\right]^2}_{\boldsymbol{\alpha}} \tag{3.18}$$

With

$$a_{c,i} = \Omega_a \frac{R^2 T_{C,i}^2}{P_{C,i}} \tag{3.19}$$

Parameters of Equations (3.18) and (3.19) are given in Table 3.3.

Table 3.3: Parameters of the attractive parameter

Equations of state	Ω_a [3.7]	κ_i
SRK	$\frac{1}{9(2^{1/3}-1)}$ ≈ 0.42748	$\kappa_i = 0.48508 + 1.551716\omega_i - 0.15613\omega_i^2$
PR	$\frac{40\eta_c + 8}{49 - 37\eta_c}$ ≈ 0.47236	$if\ \omega_i \leq 0.491$ $\kappa_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2$ $if\ \omega_i > 0.49$ $\kappa_i = 0.379642 + 1.48503\omega_i - 0.164423\omega_i^2$ $+ 0.016666\omega_i^3$

With $\eta_c = \left[1 + \sqrt[3]{4 - 2\sqrt{2}} + \sqrt[3]{4 + 2\sqrt{2}}\right]^{-1} \approx 0.253076587$ and ω the acentric factor of the component *i*.

The alpha function α(T) has a consistent monotonous decrease with increasing temperatures. Some examples are given on Figure 3.1.

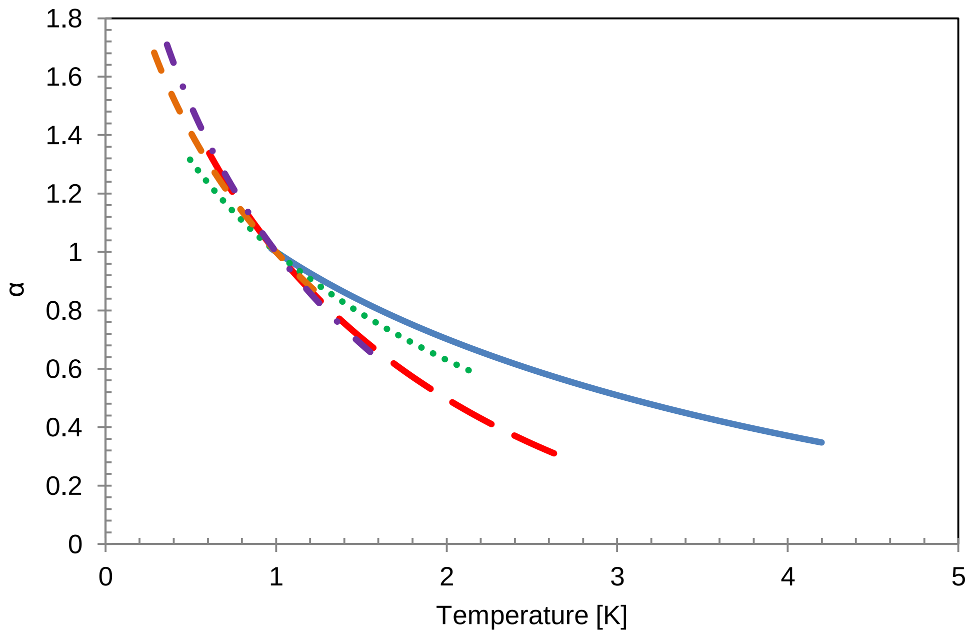


Figure 3.1: Variation of the alpha function for ▬ methane, – – carbon dioxide, ⋯ hydrogen sulphide, – – water and – · methanol.

Since the alpha function is a quadratic function, there is a minimum before an increase with increasing temperatures. For all compounds considered, the minimum is located above 1 500 K, so far beyond the domain of current industrial applications.

- Calculation of the co-volume

The co-volume for inert compounds is also an adjustable constant for the VdW EoS. The expression for the SRK and PR EoS is given below:

$$b_i^{PR} = \Omega_b \frac{RT_{C,i}}{P_{C,i}}$$

(3.20)

Table 3.4: Parameters of the co-volume

Equations of state	Ω_b [3.7]
SRK	$\frac{2^{1/3}-1}{3} \approx 0.08664$
PR	$\frac{\eta_c}{\eta_c+3} \approx 0.077796$

- **Classical mixing rules**

The equations of state presented above can be used for mixture, but it is necessary to introduce mixing rules. The classical mixing rule (or Van der Waals mixing rule) is used in this work (Equations (3.21) and (3.23)).

$$a = \sum_i \sum_j x_i x_j a_{ij}$$

(3.21)

where

$$a_{ij} = \sqrt{a_i a_j}\left(1 - k_{ij}\right)$$

(3.22)

and

$$b = \sum_i x_i b_i$$

(3.23)

where k_{ij} is the binary interaction parameter. It is usually or set to zero or equal to a constant, but can also be temperature dependent. Some correlations have already been adjusted for some binary systems (e.g. hydrocarbon mixtures **[3.8]**).

3.2.4. Vapour – Liquid – Liquid Equilibrium

The liquid-liquid equilibrium can be expressed in the same way as for the vapour-liquid equilibrium. For a vapour-liquid-liquid equilibrium (VLLE) there is an equilibrium between between two liquid phases *L* and *L'* and a vapour phase *V*. The mixture is characterized by its composition z_i, the liquid phases by the liquid composition x_i and x_i' and the vapour phase by the vapour composition y_i, where *i* is the considered compound. The material balance equations are given by Equations (3.24) and (3.25):

$$z_i = x_i L + x_i^{'} L^{'} + y_i V \tag{3.24}$$

$$1 = L + L^{'} + V \tag{3.25}$$

The equilibrium relations between the compositions are:

$$\frac{y_i}{x_i} = \frac{\phi_i^L}{\phi_i^V} \tag{3.26}$$

$$\frac{y_i}{x_i^{'}} = \frac{\phi_i^{L'}}{\phi_i^V} \tag{3.27}$$

where ϕ is the fugacity coefficient of the component *i* in the phase *j*.

Furthermore, the phase compositions have to satisfy the normalization constraints:

$$\sum_i x_i = 1 \tag{3.28}$$

$$\sum_i x_i^{'} = 1 \tag{3.29}$$

$$\sum_i y_i = 1 \tag{3.30}$$

There are *3n+1*equations and *3n+5* variables (with n the total number of components in the mixture). So if the temperature and the pressure are fixed, the equilibrium composition can be found by an iterative procedure, using the three-phase flash algorithm.

3.2.5. Hydrate Phase

The hydrate phase is modelled using the solid solution of van der Waals and Platteeuw **[3.9]**, as implemented by Parrish and Prausnitz **[3.10]**. The hydrate phase model is based on the thermodynamic equilibrium, which means equality of temperatures, pressures and fugacities. In the case of liquid water – vapour – hydrates three phases equilibrium, fugacities of each phase are then equal. The fugacity of water in the hydrate phase is expressed by Equation (3.31) **[3.11]**:

$$f_w^H = f_w^\beta exp\left(-\frac{\Delta\mu_w^{\beta-H}}{RT}\right) \tag{3.31}$$

where f^H refers to the fugacity of the hydrate lattice and f^β to the fugacity of the empty one. $\Delta\mu$ is the chemical potential difference of water between the empty lattice and the hydrate phase. It is given by the van der Waals and Platteuw model **[3.9]**.

$$\Delta\mu_w^{\beta-H} = RT\sum_m \overline{v_m} ln\left(1+\sum_j C_{mj}f_j\right) \tag{3.32}$$

where $\overline{v_m}$ is the number of cavities of type m per water molecule in the unit cell, f_j is the fugacity of the gas component j and C_{mj} the Langmuir constant. The Langmuir constants are temperature dependent and describe the potential of interaction between the encaged guest molecule and the water molecules around it. They can be defined with the following expression:

$$C_{mj}(T) = \frac{4\pi}{kT}\int_0^\infty \underbrace{exp\left(-\frac{w(r)}{kT}\right)}_{\text{Boltzmann probability factor}} r^2 dr \tag{3.33}$$

where k is the Boltzmann's constant and $w(r)$ is the spherically symmetric cell potential in the cavity (with r the radial distance from the cavity centre). Figure 3.2 shows the shape of Boltzmann probability factor in function of r. The Boltzmann factor gives the probability to find a molecule somewhere between r_1 and r_2. Most of the time, the gas molecule is located near the centre of the cavity, about 0.5 to 1 Å from the centre. Molecules presented on Figure 3.2 have bond length between 1 and 1.5 Å. The molecule is mainly rotating around the centre of the cavity **[3.12]**.

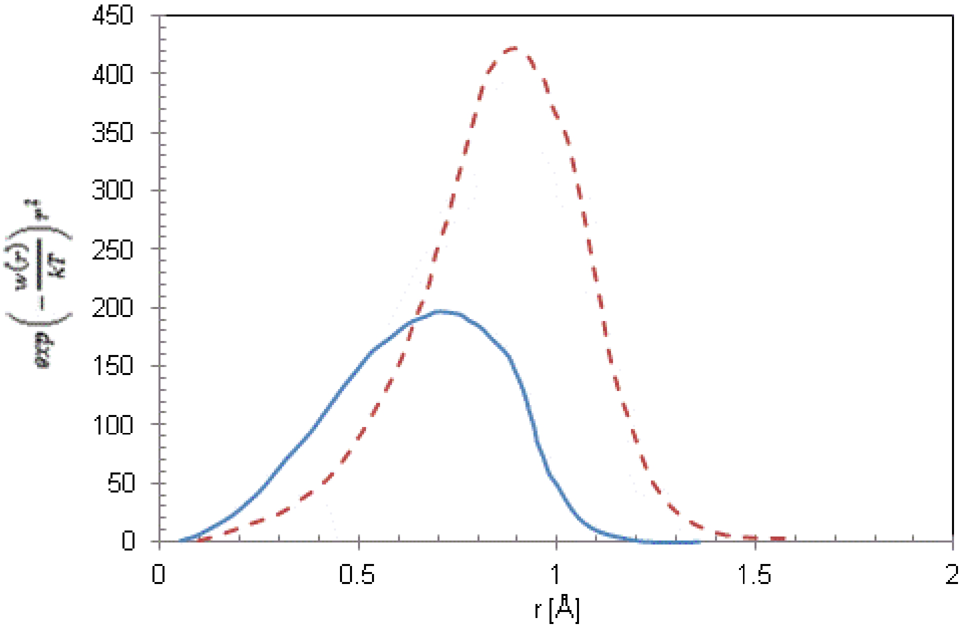


Figure 3.2: Boltzmann probability factor versus r. —— *N_2 hydrate.* - - - *C_2H_6 hydrate.* **[3.12]**

w(r) depends on the intermolecular potential function. First, the potential of interaction is based on Lennard-Jones model **[3.13]**: *Γ(r)* is defined between a host molecule and a guest molecule. Figure 3.3 shows the shape of Lennard-Jones potential, the Kihara potential is deduced by translation.

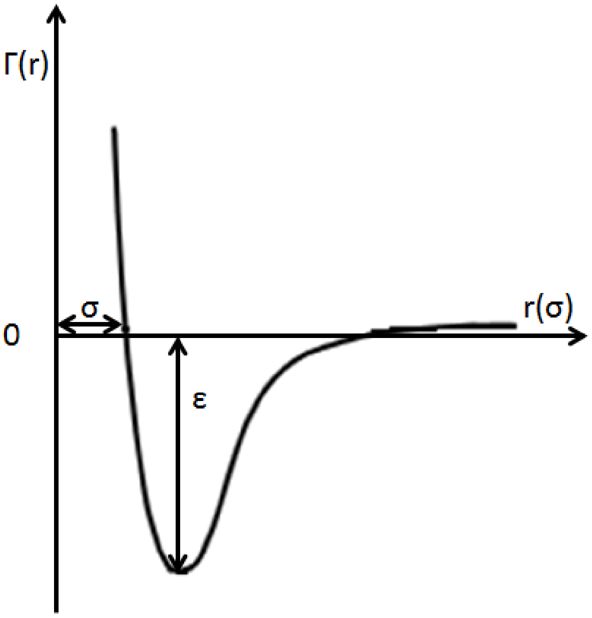


Figure 3.3: Shape of Lennard-Jones potential

Interactions between two particles are stronger when ε is deeper.

Here, the Kihara model **[3.14]** for spherical molecules has been used to calculate the potential functions, as described by McKoy and Sinanoglu **[3.12]**:

$$\Gamma(r) = \infty \qquad r \leq 2a = a_G + a_H$$
$$\Gamma(r) = 4\varepsilon\left[\left(\frac{\sigma - 2a}{r - 2a}\right)^{12} - \left(\frac{\sigma - 2a}{r - 2a}\right)^{6}\right] \qquad r > 2a$$

(3.34)

ε is the Kihara energy, a_G the radius of the guest molecule, a_H the radius of the host molecule and σ the collision diameter (the distance where Γ=0).

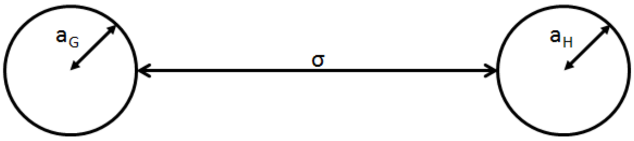


Figure 3.4: Schematic of the notation used in Kihara potential.

Kihara hard-core parameters a are given in the literature **[3.10]** and ε and σ are fitted to available experimental data of hydrate phase behaviour. These two parameters are defined in the thesis of Haghighi **[3.15]**.

Then *w(r)* is calculated as the sum of the Kihara potential on all guest-water interactions in the cavity:

$$w(r) = 2z\varepsilon\left[\frac{\sigma^{12}}{R^{11}r}\left(\delta^{10} + \frac{a}{R}\delta^{11}\right) - \frac{\sigma^{6}}{R^{5}r}\left(\delta^{4} + \frac{a}{R}\delta^{5}\right)\right]$$

(3.35)

with

$$\delta^N = \frac{1}{N}\left[\left(1 - \frac{r}{R} - \frac{a}{R}\right)^{-N} - \left(1 + \frac{r}{R} - \frac{a}{R}\right)^{-N}\right]$$

(3.36)

where Z is the number of water molecules in a cavity and R is the cavity radius.

The fugacity of water in the empty hydrate lattice is expressed by Equation (3.37).

$$f_w^\beta = f_w^{I/L} exp\left(-\frac{\Delta\mu_w^{\beta-I/L}}{RT}\right)$$

(3.37)

Where $f^{I/L}$ refers to the fugacity of pure ice or liquid water and $\Delta\mu_w^{\beta-I/L}$ is the difference between the chemical potential of the empty hydrate lattice and the one of pure liquid water (or ice). It is given by Equation (3.38).

$$\frac{\Delta\mu_w^{\beta-I/L}}{RT} = \frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^{T}\frac{\Delta h_w^{\beta-I/L}}{RT^2}dT + \int_{P_0}^{P}\frac{\Delta v_w^{\beta-I/L}}{RT}dP$$

(3.38)

Where h is the molar enthalpy, v the molar volume, μ^{β} and $\mu^{I/L}$ are respectively the chemical potential of the empty hydrate lattice and of pure liquid water (or ice). The subscript *0* refers to the triple point of water.

The difference in the enthalpy between the empty hydrate lattice and pure liquid water (or ice) is expressed as follows:

$$\Delta h_w^{\beta-I/L} = \Delta h_w^0 + \int_{T_0}^{T} \Delta C'_{pw} dT \tag{3.39}$$

Where C'_{pw} refers to the molar heat capacity (J.mol^{-1}.K^{-1}) and Δh^0 is the difference in the enthalpy between the empty hydrate lattice and pure liquid water (or ice) at the triple point.

Holder et al. **[3.16]** proposed the following expression for the heat capacity difference:

$$\Delta C'_{pw} = -37.32 + 0.179(T - T_0) \tag{3.40}$$

The reference properties for Equations (3.38) and (3.39) are given in Table 3.5.

Table 3.5: Reference properties for structures I and II hydrates

Properties	**Units**	**Structure I**	**Structure II**	**References**
$\Delta \mu_w^0$	J.mol^{-1}	1297	937	**[3.17]**
Δh_w^0	J.mol^{-1}	1389	1025	**[3.17]**
Δv_w	cm^3.mol^{-1}	3.0	3.4	**[3.10]**

3.3. INTRODUCTION TO THE CPA EQUATION OF STATE

As explained in *3.2.3*, classical equations of state are widely used in the industry. But these EoS do not take into account especially associative molecules (water, alcohols and glycols), and predictions for mixtures containing hydrogen bonding compounds can be inaccurate without readjustment of equations parameters (attractive parameter, co-volume, parameter κ_i and binary interaction parameter). Therefore, new kind of equations of state has been developed, trying to better represent associative compounds. In 1995, Kontogeorgis et al. **[3.3]** combined a cubic equation of state (SRK EoS) with the attractive term of the Wertheim's theory **[3.18-3.21]**. The cubic equation of state takes into account the physical interactions (attractive or repulsive forces) and the site-to-site attraction for associating fluids.

In this work, the SRK equation of state is replaced by the Peng-Robinson (PR) EoS **[3.2]**, justified by its better predictions for liquid density and in the critical region **[3.22]**. The PR – CPA EoS is expressed here, in term of pressure (Equation (3.41)).

$$P = \frac{RT}{v - b_i^{PR}} - \frac{a_i(T)}{v(v + b_i^{PR}) + b_i^{PR}(v - b_i^{PR})} - \frac{1}{2}\frac{RT}{v}\left(1 + \rho\frac{\partial ln(g)}{\partial \rho}\right)\sum_{i=1}^{N} x_i \sum_{A_i}(1 - X^{A_i}) \tag{3.41}$$

PR EoS parameters have already been defined in *3.2.3* for non associating compounds and the ones of the Wertheim's term are given in Table 3.6 and developed later.

Table 3.6: Parameters used in the PR-CPA EoS.

Parameters	Names	Values	Units
P	Pressure	System parameter	Pa
T	Temperature	System parameter	K
R	Ideal gas constant	8.314472	$J.mol^{-1}.K^{-1}$
v	Molar volume	System parameter	$m^3.mol^{-1}$
$\mathbf{b_i}$	Co-volume of the component i	See (3.20)	$m^3.mol^{-1}$
$\mathbf{a_i}$	Attractive parameter of the component i	See (3.18)	$J.m^3.mol^{-2}$
ρ	Density	System parameter	-
$\mathbf{x_i}$	Mole fraction of the component i	System parameter	-
$\mathbf{X^{Ai}}$	Mole fraction of the component i not bonded to the site A	See (3.42)	-

3.3.1. Hydrogen bonds

The association term in the CPA EoS represents hydrogen bonding by taking into account a specific site-site interaction. Molecules are represented as spheres. An example of spherical segments with one associating site A is shown on Figure 3.5.

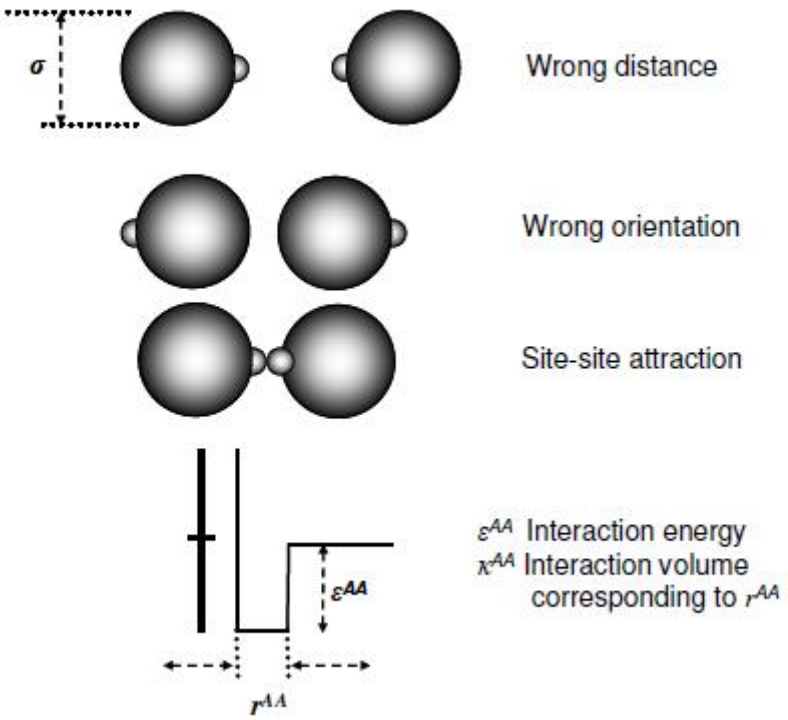


Figure 3.5: Illustration of site-to-site distance and orientation and square-well potential **[3.15]**.

The associating sites are modeled as square-well sites **[3.3]** and AA-bonded dimer is formed only when both distance and orientation are favourable. ε^{AA} is the association energy and corresponds the well depth, while κ^{AA} is the association volume and corresponds to the well width.

3.3.2. Fraction of Non-bonded Associating Molecules X^A

The association term from Wertheim's theory is the one also used in SAFT EoS. It takes into account the hydrogen bonding between associating and cross-associating compounds. It is assumed that the activity of each bonding site is independent of other bonding sites of the same molecule. Moreover, one site on a molecule cannot bond simultaneously to two sites on a different molecule and there is no double bonding between two molecules. The form of the association term is derived by Michelsen and Hendriks **[3.23]**.

In the association term, X^{A_i} is the mole fraction of sites A on molecule i that do not form bonds with other active sites B on molecules j. It is related to the association strength $\Delta^{A_iB_j}$ and the fractions X^B of all other kind of association sites B by Equation (3.42):

$$X^{A_i} = \frac{1}{1 + \rho \sum_j n_j \sum_{B_i} X^{B_i} \Delta^{A_i B_i}}$$

(3.42)

where ρ is the molar density of the fluid and x_j is the mole fraction of substance j. Both X^{A_i} and $\Delta^{A_i B_j}$ depend on the structure of the molecule and the number and type of sites. The association strength between site A on molecule i and site B on molecule j is given by Equation (3.43).

$$\Delta^{A_i B_i} = g(d) \left[exp\left(\frac{\varepsilon^{AB}}{RT}\right) - 1 \right] \beta^{A_i B_i} b$$

(3.43)

where $g(d)$ is the radial distribution function, b is the co–volume parameter from the cubic part of the model, β and ε are respectively the association energy and volume parameters of CPA. These two last parameters are adjustable.

The radial distribution is defined as:

$$g(d) = \frac{2 - \eta}{2(1 - \eta)^3}$$

(3.44)

Equation (3.44) is a derived function of Carnahan-Starling EoS **[3.24]**.

Kontogeorgis et al. (1999) **[3.3]** proposed a simplified expression of the radial distribution function $g(d)^{simpl}$ that is used in the PR-CPA EoS:

$$g(d)^{simp} = \frac{1}{1 - 1.9\eta}$$

(3.45)

where η is the reduced fluid density given as:

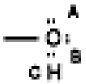
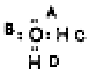
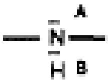
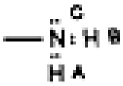
$$\eta = \frac{1}{4} b\rho = \frac{b}{4v}$$

(3.46)

where ρ is the fluid density and the co–volume parameter, b, is assumed to be temperature independent, in agreement with most published equations of state.

As seen in Equation (3.42), the association term depends on the choice of association schemes (number and type of association sites). Huang and Radosz **[3.25]** have classified eight different association schemes, presented in Table 3.7.

Table 3.7: Association schemes for associating components **[3.25]**

Species			**Rigorous type**	**Assigned type**
Acid			1	1
Alkanol			3B	2B
Water			4C	3B
Amines	**Tertiary**		1	Non self-associating
	Secondary		2B	2B
	Primary		3B	3B
Ammonia			4B	3B

In the three-site (3B) association scheme, sites A and B correspond to oxygen pairs and the site C to a hydrogen atom. The four-site (4C) association scheme has two proton donors and two proton acceptors per molecule.

The 4C and the 3B association schemes have been respectively applied for water and alcohols. Solvation is accounted for carbon dioxide. It is modelled as a non-associating compound, but it can cross-associate with water and alcohols (Figure 3.6).

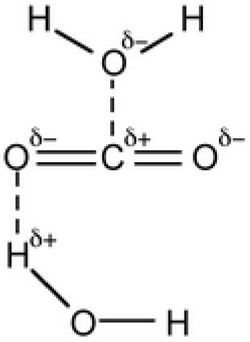


Figure 3.6: Water solvation of carbon dioxide **[3.26]**.

3.3.3. The CPA – PR Model Applied for Mixtures

The classical mixing rules as explained in *3.2.3* have been used in this work. To calculate the association strength $\Delta^{A_iB_j}$, it is necessary to calculate the association energy and volume parameters. There are calculated using combining rules. Various combining rules have been investigated **[3.27]**. Derawi et al. **[3.28]** showed that between all these rules, the CR-1 and the ECR (Elliott rule) combining rules had physical explanations: the arithmetic mean of the cross-association energy $\varepsilon^{A_iB_j}$ is proportional to the enthalpy of hydrogen bonding while the geometric mean of the cross-association volume $\beta^{A_iB_j}$ is related to the cross-entropy of the hydrogen bonding. Both combining rules give similar results, but CR-1 is the only choice for heavy alcohol-water systems **[3.29]**. Since these systems are considered in this work, the CR-1 combining rule has been employed (Equations (3.47) and (3.48)).

$$\varepsilon^{A_iB_j} = \frac{\varepsilon^{A_iB_i} + \varepsilon^{A_jB_j}}{2} \tag{3.47}$$

$$\beta^{A_iB_j} = \sqrt{\beta^{A_iB_i}\beta^{A_jB_j}} \tag{3.48}$$

The modified combining rule mCR-1 is applied for carbon dioxide with water and alcohols. The association energy has been taken from the literature **[3.30]**. The values for CO_2-H_2O and CO_2-alcohol mixtures are respectively -14 200 J/mol and -12 380 J/mol. The volume parameter has been fitted to experimental data.

3.4. INTRODUCTION TO THE PPR78 MODEL

From 2004, Jaubert et al. **[3.4]** develop a predictive method to estimate the temperature dependent binary interaction parameters $k_{ij}(T)$, through a group contribution method, based on Abdoul et al. work **[3.31]**. This new model was called PPR78 EoS, for predictive Peng-Robinson EoS.

In their work, the binary interaction parameter k_{ij} is temperature dependent. It is commonly assumed that temperature has an effect on k_{ij}. For light alkanes and CO_2-alkanes systems, the temperature dependence is quadratic with respect to $1/T$ **[3.32]**. The example of the methane-propane system is given on Figure 3.7. Two other systems are also presented: the pentane-toluene system, which has a similar volatility at low pressures, and an asymmetric system toluene-*n*-dodecane (very different volatility). For these two systems, the trend is not quadratic anymore, but the temperature dependence of the k_{ij} parameter is confirmed.

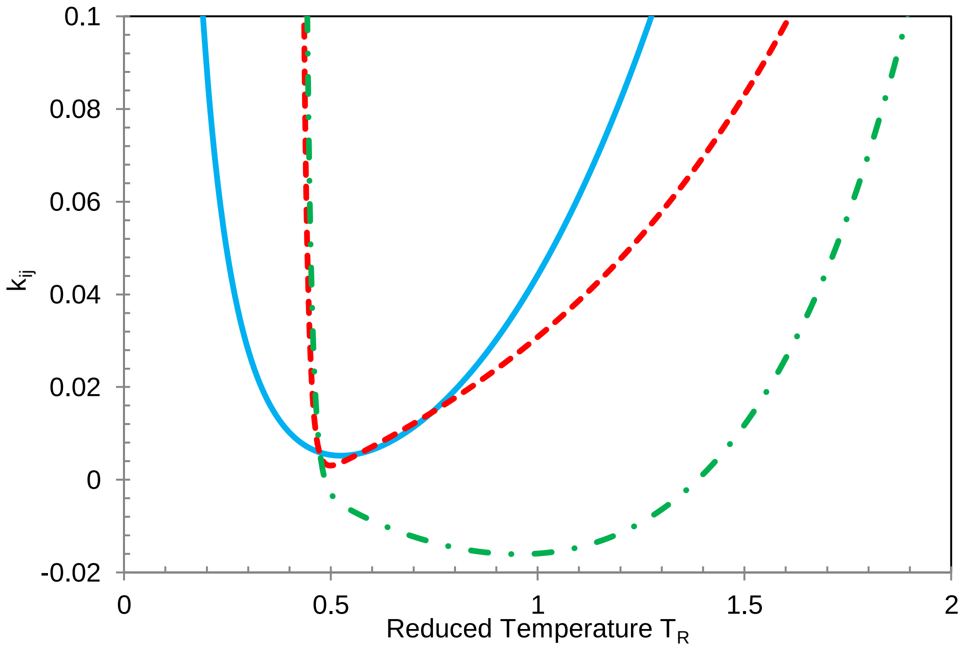


Figure 3.7: Temperature dependence of the kij parameter. ━━ *Methane-propane system.* ⋯⋯ *Pentane-toluene system..* ━ · *Toluene-dodecane system.* T_R *is the reduced temperature of propane and toluene.* k_{ij} *calculated with Equation (3.49)*

The binary interaction parameter defined by Qian et al. **[3.33]** can be calculated for any systems containing the groups presented in Table 3.8.

Table 3.8: Groups defined in the PPR78 EoS.

Families	**Groups**	**References**
Alkanes	CH_3	**[3.4]**
	CH_2	
	CH	
	CH_4	
	C_2H_6	
Aromatics	CH_{aro}	**[3.34]**
	C_{aro}	
	$C_{\text{fused aromatic rings}}$	
Napthenics	$CH_{2,cyclic}$	**[3.35]**
	CH_{cyclic} or C_{cyclic}	
Alkenes	C_2H_4	**[3.36]**
	$CH_{2,alk}$ or CH_{alk}	
	C_{alk}	
	$CH_{cyclic,alk}$ or $C_{cyclic,alk}$	
Inert gases	CO_2	**[3.37]**
	N_2	**[3.38]**
	H_2S	**[3.39]**
	SH	**[3.40, 3.41]**
	H_2	**[3.42]**
Water	H_2O	**[3.33]**

The binary interaction parameter is given by Equation (3.49).

$$k_{ij}(T) = \frac{-\frac{1}{2}\times Sum_{PPR78} - \left(\frac{\sqrt{\alpha_i(T)}}{b_i} - \frac{\sqrt{\alpha_j(T)}}{b_j}\right)^2}{2\frac{\sqrt{\alpha_i(T)\alpha_j(T)}}{b_i b_j}} \tag{3.49}$$

With

$$Sum_{PPR78} = \sum_{k=1}^{Ng}\sum_{l=1}^{Ng}(\alpha_{ik}-\alpha_{jk})(\alpha_{il}-\alpha_{jl})A_{kl}\left(\frac{298.15}{T}\right)^{\left(\frac{B_{kl}}{A_{kl}}-1\right)} \tag{3.50}$$

Where

$$\alpha_{ik} = \frac{number\ of\ group\ k\ in\ molecule\ i}{total\ number\ of\ groups\ in\ molecule\ i}$$

and A_{kl} and B_{kl} are group interaction parameters reported in the last manuscript of Qian et al. (2013) **[3.33]**.

To adjust their parameters, Jaubert et al. defined the objective function by the following equation:

$$F_{obj} = \frac{F_{obj,bubble} + F_{obj,dew} + F_{obj,crit.comp} + F_{obj,crit.pressure}}{n_{bubble} + n_{dew} + n_{crit} + n_{crit}} \tag{3.51}$$

with

$$F_{obj,bubble} = 100 \sum_{i=1}^{n_{bubble}} 0.5 \left(\frac{\left|x_{1,exp} - x_{1,calc}\right|}{x_{1,exp}} + \frac{\left|x_{2,exp} - x_{2,calc}\right|}{x_{2,exp}} \right)_i$$

$$F_{obj,dew} = 100 \sum_{i=1}^{n_{dew}} 0.5 \left(\frac{\left|y_{1,exp} - y_{1,calc}\right|}{y_{1,exp}} + \frac{\left|y_{2,exp} - y_{2,calc}\right|}{y_{2,exp}} \right)_i$$

$$F_{obj,crit.comp} = 100 \sum_{i=1}^{n_{crit}} 0.5 \left(\frac{\left|x_{C1,exp} - x_{C1,calc}\right|}{x_{C1,exp}} + \frac{\left|x_{C2,exp} - x_{C2,calc}\right|}{x_{C2,exp}} \right)_i$$

$$F_{obj,crit.pressure} = 100 \sum_{i=1}^{n_{crit}} 0.5 \left(\frac{\left|P_{Cm,exp} - P_{Cm,calc}\right|}{P_{Cm,exp}} \right)_i$$

where n_{bubble}, n_{dew} and n_{crit} are the number of bubble points, dew points and mixture critical points. P_{Cm} is the binary critical pressure. Later on, they also took into account mixing enthalpies and heats of mixing in terms of temperature effect **[3.43]**:

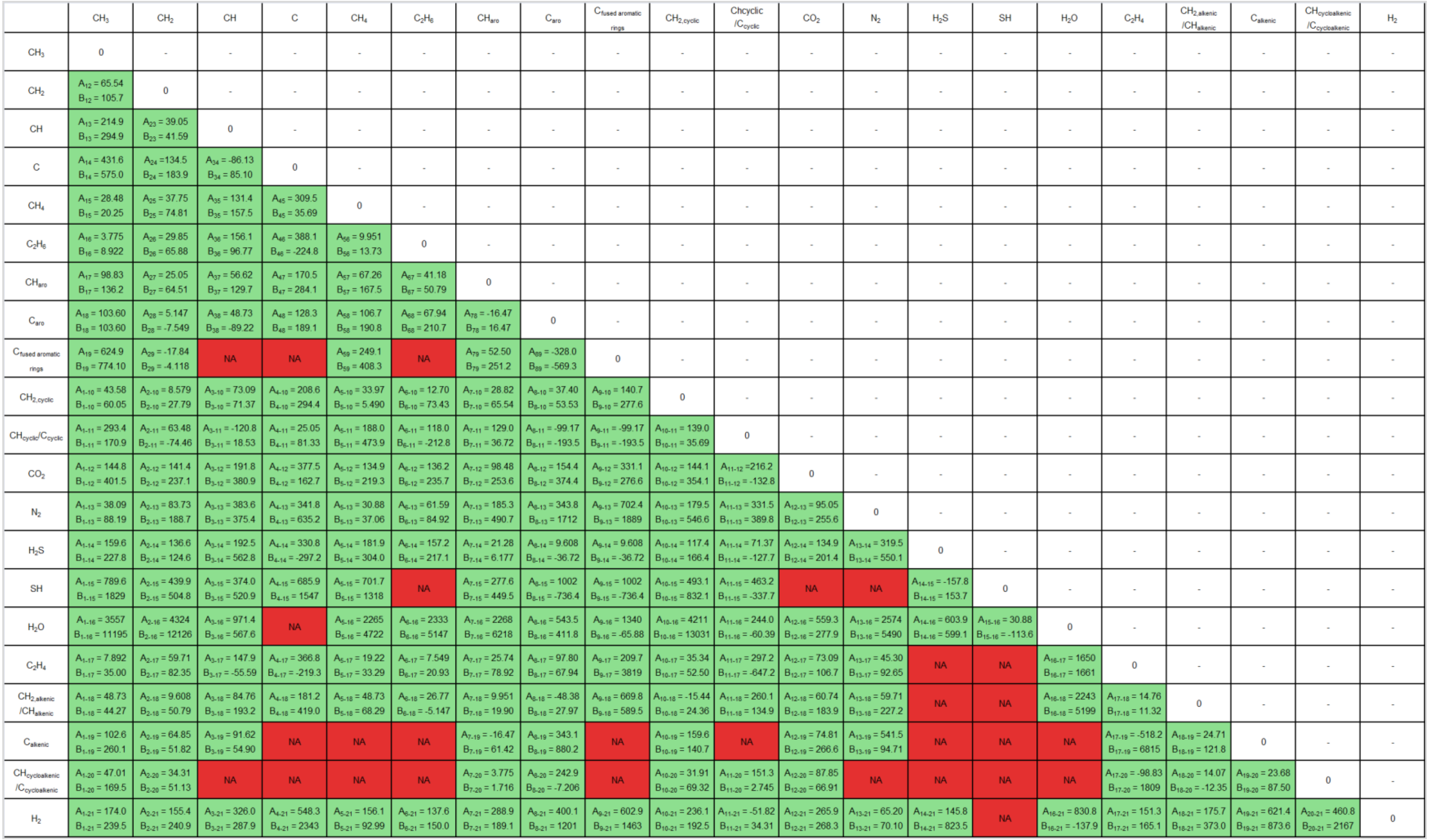
$$\overline{\Delta T_h} = \frac{1}{n_h} \sum_{i=1}^{n_h} (\Delta T_h)_i \tag{3.52}$$

Where

$$\Delta T_h = \frac{\Delta h^M}{z_1 c_{p,pure\ 1} + z_2 c_{p,pure\ 2} + c_p^M} \tag{3.53}$$

Parameters A_{kl} and B_{kl} are presented in Table 3.9.

Table 3.9: Group parameters in the PPR78 EoS. Green: parameters available. Red: no parameters



	CH_3	CH_2	CH	C	CH_4	C_2H_6	CH_{aro}	C_{aro}	$C_{fused\ aromatic\ rings}$	$CH_{2,cyclic}$	Chcyclic /C_{cyclic}	CO_2	N_2	H_2S	SH	H_2O	C_2H_4	$CH_{2,alkenic}$ /$CH_{alkenic}$	$C_{alkenic}$	$CH_{cycloalkenic}$ /$C_{cycloalkenic}$	H_2
CH_3	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CH_2	A_{12} = 65.54 B_{12} = 105.7	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CH	A_{13} = 214.9 B_{13} = 294.9	A_{23} = 39.05 B_{23} = 41.59	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C	A_{14} = 431.6 B_{14} = 575.0	A_{24} =134.5 B_{24} = 183.9	A_{34} = -86.13 B_{34} = 85.10	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CH_4	A_{15} = 28.48 B_{15} = 20.25	A_{25} = 37.75 B_{25} = 74.81	A_{35} = 131.4 B_{35} = 157.5	A_{45} = 309.5 B_{45} = 35.69	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C_2H_6	A_{16} = 3.775 B_{16} = 8.922	A_{26} = 29.85 B_{26} = 65.88	A_{36} = 156.1 B_{36} = 96.77	A_{46} = 388.1 B_{46} = -224.8	A_{56} = 9.951 B_{56} = 13.73	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CH_{aro}	A_{17} = 98.83 B_{17} = 136.2	A_{27} = 25.05 B_{27} = 64.51	A_{37} = 56.62 B_{37} = 129.7	A_{47} = 170.5 B_{47} = 284.1	A_{57} = 67.26 B_{57} = 167.5	A_{67} = 41.18 B_{67} = 50.79	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C_{aro}	A_{18} = 103.60 B_{18} = 103.60	A_{28} = 5.147 B_{28} = -7.549	A_{38} = 48.73 B_{38} = -89.22	A_{48} = 128.3 B_{48} = 189.1	A_{58} = 106.7 B_{58} = 190.8	A_{68} = 67.94 B_{68} = 210.7	A_{78} = -16.47 B_{78} = 16.47	0	-	-	-	-	-	-	-	-	-	-	-	-	-
$C_{fused\ aromatic\ rings}$	A_{19} = 624.9 B_{19} = 774.10	A_{29} = -17.84 B_{29} = -4.118	NA	NA	A_{59} = 249.1 B_{59} = 408.3	NA	A_{79} = 52.50 B_{79} = 251.2	A_{89} = -328.0 B_{89} = -569.3	0	-	-	-	-	-	-	-	-	-	-	-	-
$CH_{2,cyclic}$	A_{1-10} = 43.58 B_{1-10} = 60.05	A_{2-10} = 8.579 B_{2-10} = 27.79	A_{3-10} = 73.09 B_{3-10} = 71.37	A_{4-10} = 208.6 B_{4-10} = 294.4	A_{5-10} = 33.97 B_{5-10} = 5.490	A_{6-10} = 12.70 B_{6-10} = 73.43	A_{7-10} = 28.82 B_{7-10} = 65.54	A_{8-10} = 37.40 B_{8-10} = 53.53	A_{9-10} = 140.7 B_{9-10} = 277.6	0	-	-	-	-	-	-	-	-	-	-	-
CH_{cyclic}/C_{cyclic}	A_{1-11} = 293.4 B_{1-11} = 170.9	A_{2-11} = 63.48 B_{2-11} = -74.46	A_{3-11} = -120.8 B_{3-11} = 18.53	A_{4-11} = 25.05 B_{4-11} = 81.33	A_{5-11} = 188.0 B_{5-11} = 473.9	A_{6-11} = 118.0 B_{6-11} = -212.8	A_{7-11} = 129.0 B_{7-11} = 36.72	A_{8-11} = -99.17 B_{8-11} = -193.5	A_{9-11} = -99.17 B_{9-11} = -193.5	A_{10-11} = 139.0 B_{10-11} = 35.69	0	-	-	-	-	-	-	-	-	-	-
CO_2	A_{1-12} = 144.8 B_{1-12} = 401.5	A_{2-12} = 141.4 B_{2-12} = 237.1	A_{3-12} = 191.8 B_{3-12} = 380.9	A_{4-12} = 377.5 B_{4-12} = 162.7	A_{5-12} = 134.9 B_{5-12} = 219.3	A_{6-12} = 136.2 B_{6-12} = 235.7	A_{7-12} = 98.48 B_{7-12} = 253.6	A_{8-12} = 154.4 B_{8-12} = 374.4	A_{9-12} = 331.1 B_{9-12} = 276.6	A_{10-12} = 144.1 B_{10-12} = 354.1	A_{11-12} =216.2 B_{11-12} = -132.8	0	-	-	-	-	-	-	-	-	-
N_2	A_{1-13} = 38.09 B_{1-13} = 88.19	A_{2-13} = 83.73 B_{2-13} = 188.7	A_{3-13} = 383.6 B_{3-13} = 375.4	A_{4-13} = 341.8 B_{4-13} = 635.2	A_{5-13} = 30.88 B_{5-13} = 37.06	A_{6-13} = 61.59 B_{6-13} = 84.92	A_{7-13} = 185.3 B_{7-13} = 490.7	A_{8-13} = 343.8 B_{8-13} = 1712	A_{9-13} = 702.4 B_{9-13} = 1889	A_{10-13} = 179.5 B_{10-13} = 546.6	A_{11-13} = 331.5 B_{11-13} = 389.8	A_{12-13} = 95.05 B_{12-13} = 255.6	0	-	-	-	-	-	-	-	-
H_2S	A_{1-14} = 159.6 B_{1-14} = 227.8	A_{2-14} = 136.6 B_{2-14} = 124.6	A_{3-14} = 192.5 B_{3-14} = 562.8	A_{4-14} = 330.8 B_{4-14} = -297.2	A_{5-14} = 181.9 B_{5-14} = 304.0	A_{6-14} = 157.2 B_{6-14} = 217.1	A_{7-14} = 21.28 B_{7-14} = 6.177	A_{8-14} = 9.608 B_{8-14} = -36.72	A_{9-14} = 9.608 B_{9-14} = -36.72	A_{10-14} = 117.4 B_{10-14} = 166.4	A_{11-14} = 71.37 B_{11-14} = -127.7	A_{12-14} = 134.9 B_{12-14} = 201.4	A_{13-14} = 319.5 B_{13-14} = 550.1	0	-	-	-	-	-	-	-
SH	A_{1-15} = 789.6 B_{1-15} = 1829	A_{2-15} = 439.9 B_{2-15} = 504.8	A_{3-15} = 374.0 B_{3-15} = 520.9	A_{4-15} = 685.9 B_{4-15} = 1547	A_{5-15} = 701.7 B_{5-15} = 1318	NA	A_{7-15} = 277.6 B_{7-15} = 449.5	A_{8-15} = 1002 B_{8-15} = -736.4	A_{9-15} = 1002 B_{9-15} = -736.4	A_{10-15} = 493.1 B_{10-15} = 832.1	A_{11-15} = 463.2 B_{11-15} = -337.7	NA	NA	A_{14-15} = -157.8 B_{14-15} = 153.7	0	-	-	-	-	-	-
H_2O	A_{1-16} = 3557 B_{1-16} = 11195	A_{2-16} = 4324 B_{2-16} = 12126	A_{3-16} = 971.4 B_{3-16} = 567.6	NA	A_{5-16} = 2265 B_{5-16} = 4722	A_{6-16} = 2333 B_{6-16} = 5147	A_{7-16} = 2268 B_{7-16} = 6218	A_{8-16} = 543.5 B_{8-16} = 411.8	A_{9-16} = 1340 B_{9-16} = -65.88	A_{10-16} = 4211 B_{10-16} = 13031	A_{11-16} = 244.0 B_{11-16} = -60.39	A_{12-16} = 559.3 B_{12-16} = 277.9	A_{13-16} = 2574 B_{13-16} = 5490	A_{14-16} = 603.9 B_{14-16} = 599.1	A_{15-16} = 30.88 B_{15-16} = -113.6	0	-	-	-	-	-
C_2H_4	A_{1-17} = 7.892 B_{1-17} = 35.00	A_{2-17} = 59.71 B_{2-17} = 82.35	A_{3-17} = 147.9 B_{3-17} = -55.59	A_{4-17} = 366.8 B_{4-17} = -219.3	A_{5-17} = 19.22 B_{5-17} = 33.29	A_{6-17} = 7.549 B_{6-17} = 20.93	A_{7-17} = 25.74 B_{7-17} = 78.92	A_{8-17} = 97.80 B_{8-17} = 67.94	A_{9-17} = 209.7 B_{9-17} = 3819	A_{10-17} = 35.34 B_{10-17} = 52.50	A_{11-17} = 297.2 B_{11-17} = -647.2	A_{12-17} = 73.09 B_{12-17} = 106.7	A_{13-17} = 45.30 B_{13-17} = 92.65	NA	NA	A_{16-17} = 1650 B_{16-17} = 1661	0	-	-	-	-
$CH_{2,alkenic}$ /$CH_{alkenic}$	A_{1-18} = 48.73 B_{1-18} = 44.27	A_{2-18} = 9.608 B_{2-18} = 50.79	A_{3-18} = 84.76 B_{3-18} = 193.2	A_{4-18} = 181.2 B_{4-18} = 419.0	A_{5-18} = 48.73 B_{5-18} = 68.29	A_{6-18} = 26.77 B_{6-18} = -5.147	A_{7-18} = 9.951 B_{7-18} = 19.90	A_{8-18} = -48.38 B_{8-18} = 27.97	A_{9-18} = 669.8 B_{9-18} = 589.5	A_{10-18} = -15.44 B_{10-18} = 24.36	A_{11-18} = 260.1 B_{11-18} = 134.9	A_{12-18} = 60.74 B_{12-18} = 183.9	A_{13-18} = 59.71 B_{13-18} = 227.2	NA	NA	A_{16-18} = 2243 B_{16-18} = 5199	A_{17-18} = 14.76 B_{17-18} = 11.32	0	-	-	-
$C_{alkenic}$	A_{1-19} = 102.6 B_{1-19} = 260.1	A_{2-19} = 64.85 B_{2-19} = 51.82	A_{3-19} = 91.62 B_{3-19} = 54.90	NA	NA	NA	A_{7-19} = -16.47 B_{7-19} = 61.42	A_{8-19} = 343.1 B_{8-19} = 880.2	NA	A_{10-19} = 159.6 B_{10-19} = 140.7	NA	A_{12-19} = 74.81 B_{12-19} = 266.6	A_{13-19} = 541.5 B_{13-19} = 94.71	NA	NA	NA	A_{17-19} = -518.2 B_{17-19} = 6815	A_{18-19} = 24.71 B_{18-19} = 121.8	0	-	-
$CH_{cycloalkenic}$ /$C_{cycloalkenic}$	A_{1-20} = 47.01 B_{1-20} = 169.5	A_{2-20} = 34.31 B_{2-20} = 51.13	NA	NA	NA	NA	A_{7-20} = 3.775 B_{7-20} = 1.716	A_{8-20} = 242.9 B_{8-20} = -7.206	NA	A_{10-20} = 31.91 B_{10-20} = 69.32	A_{11-20} = 151.3 B_{11-20} = 2.745	A_{12-20} = 87.85 B_{12-20} = 66.91	NA	NA	NA	NA	A_{17-20} = -98.83 B_{17-20} = 1809	A_{18-20} = 14.07 B_{18-20} = -12.35	A_{19-20} = 23.68 B_{19-20} = 87.50	0	-
H_2	A_{1-21} = 174.0 B_{1-21} = 239.5	A_{2-21} = 155.4 B_{2-21} = 240.9	A_{3-21} = 326.0 B_{3-21} = 287.9	A_{4-21} = 548.3 B_{4-21} = 2343	A_{5-21} = 156.1 B_{5-21} = 92.99	A_{6-21} = 137.6 B_{6-21} = 150.0	A_{7-21} = 288.9 B_{7-21} = 189.1	A_{8-21} = 400.1 B_{8-21} = 1201	A_{9-21} = 602.9 B_{9-21} = 1463	A_{10-21} = 236.1 B_{10-21} = 192.5	A_{11-21} = -51.82 B_{11-21} = 34.31	A_{12-21} = 265.9 B_{12-21} = 268.3	A_{13-21} = 65.20 B_{13-21} = 70.10	A_{14-21} = 145.8 B_{14-21} = 823.5	NA	A_{16-21} = 830.8 B_{16-21} = -137.9	A_{17-21} = 151.3 B_{17-21} = 165.1	A_{18-21} = 175.7 B_{18-21} = 373.0	A_{19-21} = 621.4 B_{19-21} = 873.6	A_{20-21} = 460.8 B_{20-21} = 2167	0

CONCLUSION

Two thermodynamic approaches enable to describe phase equilibrium: the symmetric and dissymmetric approaches. In both cases, it is necessary to select an equation of state. Among all equations already defined, two of them have been taken on: the CPA and the PPR78 EoS. The first one is suitable for associating compounds and the second one has a predictive feature. Considering the advantages of a predictive model and the good results obtained by Jaubert and co-workers, it has been decided to include their group contribution approach to the CPA EoS.

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CHAPTER 4 - THE GC-PR-CPA MODEL

Dans le cadre de cette thèse, un nouveau modèle, appelé GC-PR-CPA, a été établi. L'équation d'état Cubic-Plus-Association (CPA), qui réunit une équation d'état cubique au terme associatif de Wertheim, est combinée au modèle de contribution de groupe Predictive Peng-Robinson (PPR78), qui évalue de façon prédictive les coefficients d'interaction binaire. Dans un premier temps, les paramètres des corps purs eau et alcools (methanol à n-decanol) de l'équation d'état PR-CPA ont été réjustés sur des données de pression de vapeur staturante et de densité liquide (extraites du NIST). Ensuite la formulation du paramètre d'interaction binaire a été modifiée. Enfin, les paramètres d'interaction entre groupes ont été ajustés sur des données d'équilibre présentées dans les annexes A1 à A18.

4.1. INTRODUCTION

In this work, the Group Contribution – Peng-Robinson – Cubic-Plus-Association (GC-PR-CPA) model has been developed, by combining the PR-Cubic-Plus-Association (CPA) EoS **[4.1]** and the Predictive Peng-Robinson (PPR78) EoS **[4.2]**.

Group parameters defined in the PPR78 EoS, except the ones for water, have been implemented and used in the new model. Hydrocarbons and inert gases are considered as non-associative compounds and in these cases the PR-CPA EoS is reduced to the PR EoS. Moreover, even if the group H_2O has been recently added to the PPR78 model **[4.3]**, quantitative predictions are considered not accurate enough. With an adjusted binary interaction parameter, the CPA EoS gives already good predictions for systems with water. The idea in this work is to have a predictive approach while maintaining accurate predictions of the CPA EoS for associating compounds.

4.2. Pure Compounds

Unlike for inert compounds, the expressions given by Equations (3.18) and (3.20) are not appropriate for associating compounds. Therefore the attractive parameter, the co-volume and the association parameters (energy and volume) are fitted to vapour pressure and saturated liquid density data. Adjustments have been made for water and normal alcohols up to n-decanol (Table 4.1) using TPure, software developed in the Centre Thermodynamic of Processes (CTP).

Table 4.1: PR-CPA parameters for water and alcohol

Components	**a_0** **[bar.L^2.mol^{-2}]**	**b** **[L.mol^{-1}]**	**C_1**	**ε** **[bar.L.mol^{-1}]**	**β** **[10^3]**	**Temperature range [K]**	**ΔP** **[%]**	**Δρ** **[%]**
Water	2.174	0.015	0.639	146.39	68.31	273 – 643	1.1	2.7
Methanol	4.929	0.032	0.770	201.75	40.20	176 – 506	0.9	1.1
Ethanol	8.387	0.048	0.654	237.98	8.47	260 – 510	0.3	0.8
Propanol	14.72	0.065	0.849	207.66	5.58	202 – 527	0.8	1.1
Butanol	19.77	0.081	0.769	236.11	2.74	205 – 555	1.7	2.0
Pentanol	26.20	0.098	1.183	155.25	5.58	250 – 500	1.9	0.9
Hexanol	31.70	0.114	1.292	138.57	5.74	250 – 500	1.2	0.8
Heptanol	39.85	0.132	1.077	244.72	0.417	250 – 500	0.9	1.3
Octanol	44.32	0.148	1.349	201.39	0.644	250 – 500	1.5	1.4
Nonanol	51.29	0.164	1.361	262.46	0.074	250 – 500	1.4	1.0
Decanol	57.68	0.183	1.450	246.39	0.091	260 – 500	1.3	1.5

4.3. Group Interaction Parameters

Binary interaction parameters are calculated using a predictive approach, based on the PPR78 model. The binary interaction parameter defined in the PPR78 model has been modified for binary systems with associating compounds. Then group interaction parameters have been adjusted for these systems using equilibrium data, listed in Appendices A1 to A18.

4.3.1. Addition of the Group H_2O

First, the group H_2O has been added to the GC-PR-CPA model. Group parameters have been adjusted on literature data and using the flash calculation of the Hydraflash™ software. The objective function defined by Equation (4.1) has been minimized using the simplex algorithm.

$$F = \frac{1}{NEXP} \sum_{i=1}^{NEXP} \left(\frac{x_{i,exp} - x_{i,calc}}{0.01 \times \left(1 + x_{i,exp}\right)} \right)^2 \tag{4.1}$$

where N_{EXP} is the number of experimental data, $x_{i,exp}$ the experimental liquid mole fraction of the component i and $x_{i,calc}$ the calculated one.

The objective function was limited to solubility data, because they are more widely available in the literature. Indeed, in the case of VLE, measuring gas solubility is easier than measuring the water content. Furthermore, the binary interaction parameter for systems with water does not impact on water content in gas phase (Figure 4.2). However, as shown on Figure 4.1, for the system methane – water, the SRK-CPA EoS with a k_{ij} set to zero over predicts methane solubility, while the SRK-CPA EoS with polynomial binary interaction parameters is in good agreement with experimental data. Therefore, adjusting the binary interaction parameter improves solubility predictions.

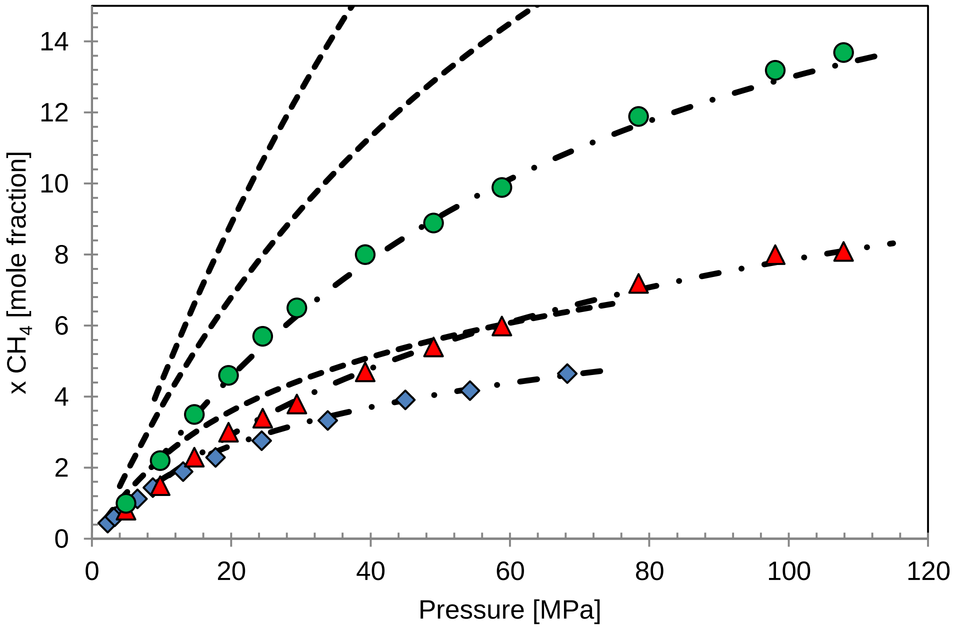

Figure 4.1: CH_4 solubility in water at 310.93 K (♦) **[4.4]**, *423.15 K (▲) and 473.15 K (●)* **[4.5]**. *▬ ▬ SRK–CPA EoS with k_{ij}=0. ▬ ▪ SRK–CPA EoS with adjusted k_{ij}.*

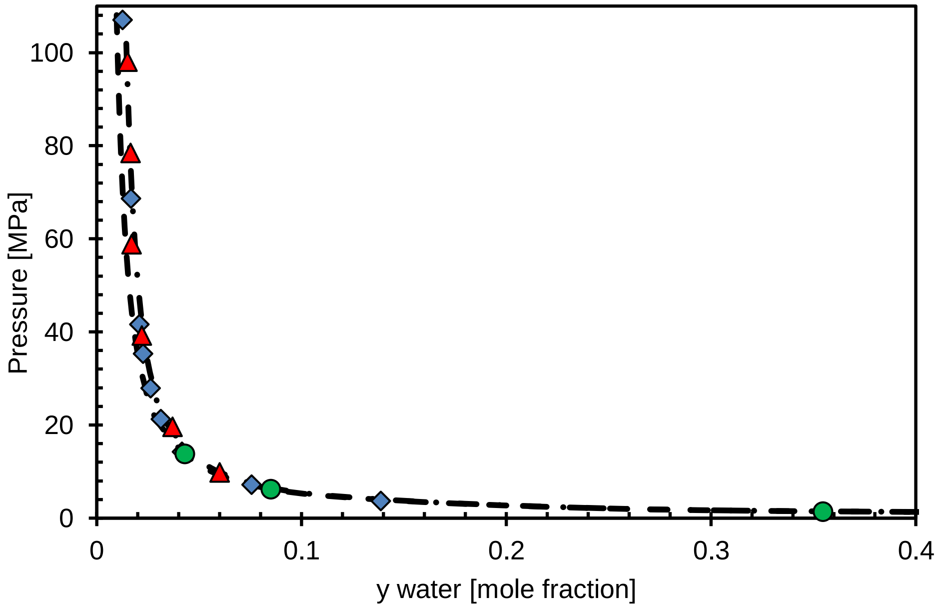

Figure 4.2: Water content in the vapour phase of the methane and water binary system at 423.15K (♦) **[4.6]**, *(▲)* **[4.5]** *and (●)* **[4.7]**. *▬ ▬ SRK–CPA EoS with k_{ij}=0. ▬ ▪ SRK–CPA EoS with adjusted k_{ij}.*

Binary interaction parameters have been also adjusted on literature data temperature by temperature for the methane – water, ethane – water, carbon dioxide – water, nitrogen – water and benzene-water systems. They present a polynomial tendency (Figure 4.3 and Figure 4.4) similar to a Henry's law constant **[4.8]**. Initially, the binary interaction parameter as defined in the PPR78 EoS (Equation (3.50)) has been used, but results were not satisfactory and the polynomial trend could not be reproduced.

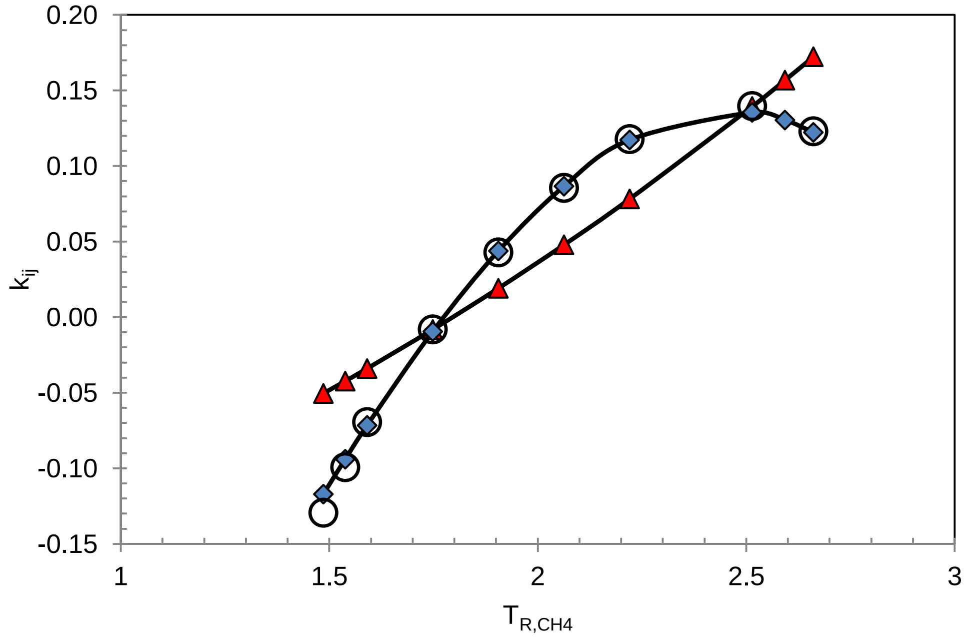

Figure 4.3: Shape of the methane – water k_{ij} versus methane reduced temperature T_R. -○- Adjusted k_{ij}. -◆- GC–PR–CPA k_{ij} (4.2). -▲- PR–CPA with PPR78 k_{ij} (3.50).

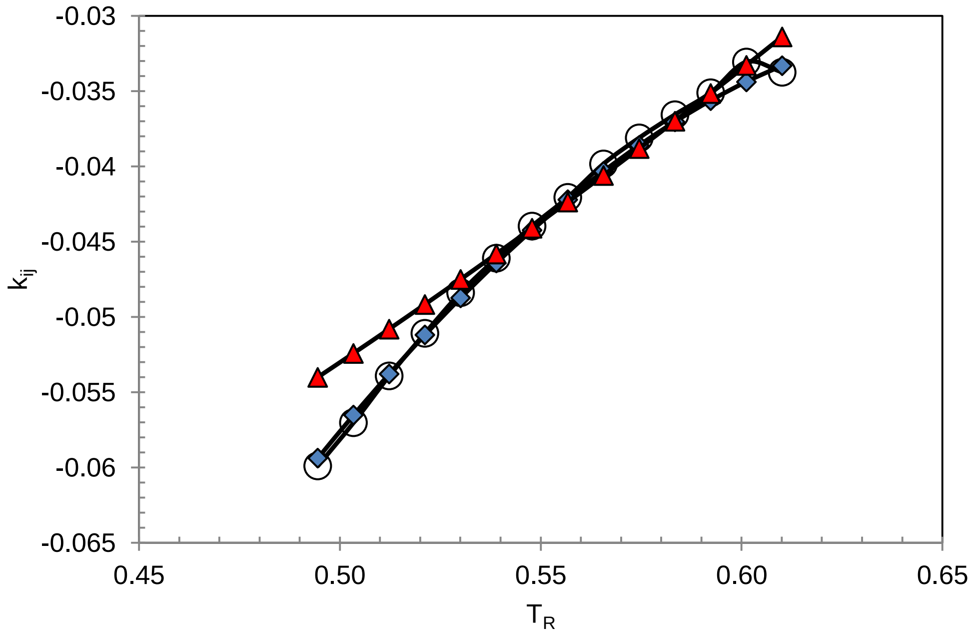

Figure 4.4: Shape of the benzene – water k_{ij} versus benzene reduced temperature T_R. -○- Adjusted k_{ij}. -◆- GC–PR–CPA k_{ij} (4.2). -▲- PR–CPA with PPR78 k_{ij} (3.50).

Therefore the term Sum_{PPR78} has been modified for the group H_2O under a second order polynomial expression: three new interaction parameters C_{kH2O}, D_{kH2O} and E_{kH2O} have been introduced (Equation (4.2)).

$$Sum_{asso} = \sum_{k=1}^{H_2O} (\alpha_{ik} - \alpha_{jk})(\alpha_{iH_2O} - \alpha_{jH_2O})(C_{kH_2O}T^2 + D_{kH_2O}T + E_{kH_2O})$$
$$+ \sum_{l=1}^{H_2O} (\alpha_{iH_2O} - \alpha_{jH_2O})(\alpha_{il} - \alpha_{jl})\,(C_{H_2Ol}T^2 + D_{H_2Ol}T + E_{H_2Ol}) \tag{4.2}$$

With $C_{k,H2O}=C_{H2O,l}$, $D_{k,H2O}=D_{H2O,l}$, $E_{k,H2O}=E_{H2O,l}$.

The two predictive binary interaction parameters have been compared to the adjusted one for the methane – water system (Table 4.2) and the benzene-water system (Table 4.3).

Table 4.2: Comparison between adjusted k_{ij} temperature by temperature, calculated k_{ij} with PPR78 and calculated k_{ij} with the GC-PR-CPA EoS for the binary system methane-water.

Temperatures [K]	**Adjusted k_{ij}**	**Calculated k_{ij} with (4.2)**	***AAD [%]***	**Calculated k_{ij} with (3.50)**	***AAD [%]***
283	-0.129	-0.117	*9*	-0.050	*67*
293	-0.099	-0.094	*5*	-0.042	*61*
303	-0.069	-0.072	*3*	-0.034	*49*
333	-0.008	-0.0095	*18*	-0.008	*1*
363	0.043	0.044	*2*	0.019	*54*
393	0.086	0.087	*1*	0.048	*43*
423	0.118	0.117	*0*	0.078	*34*
479	0.140	0.136	*3*	0.139	*0*
507	0.123	0.122	*1*	0.172	*40*

Table 4.3: Comparison between adjusted k_{ij} temperature by temperature, calculated k_{ij} with PPR78 and calculated k_{ij} with the GC-PR-CPA EoS for the binary system benzene-water.

Temperatures [K]	**Adjusted k_{ij}**	**Calculated k_{ij} with (4.2)**	***AAD [%]***	**Calculated k_{ij} with (3.50)**	***AAD [%]***
278	-0.060	-0.059	*1*	-0.054	*10*
283	-0.057	-0.056	*1*	-0.052	*8*
288	-0.054	-0.054	*1*	-0.051	*6*
293	-0.051	-0.051	*0*	-0.049	*4*
298	-0.048	-0.048	*0*	-0.048	*2*
303	-0.046	-0.046	*0*	-0.046	*1*
308	-0.044	-0.044	*0*	-0.044	*0*
313	-0.042	-0.042	*1*	-0.042	*1*
318	-0.040	-0.040	*0*	-0.041	*2*
323	-0.038	-0.038	*0*	-0.039	*2*
328	-0.037	-0.037	*1*	-0.037	*1*
333	-0.035	-0.035	*1*	-0.035	*0*
338	-0.033	-0.034	*4*	-0.033	*1*
343	-0.034	-0.033	*1*	-0.031	*7*

The GC-PR-CPA model is able to reproduce with more accuracy the trend of the k_{ij} parameter.

The model proposed has therefore five parameters: two parameters (A_{kl} and B_{kl}) for non-associating groups and three parameters (C_{kl}, D_{kl} and E_{kl}) for associating groups such as water. Therefore, if a binary system without associating compounds is studied, the model is reduced to the PPR78 EoS: the associating part of the PR-CPA EoS is not useful and the binary interaction parameter is the one defined by Equation (3.49) with the term Sum_{PPR78}. However, for a system with water, the PR-CPA EoS is applied and the binary interaction parameter is calculated with Equation (3.49) together with the new term Sum_{asso} (Equation (4.2)). Table 4.4 presents the group interaction parameters with water obtained with Equation (4.2).

Table 4.4: Group interaction parameters with water

Groups (k)	**$C_{k,H2O}$** [10^3 Pa.K^{-2}]	**$D_{k,H2O}$** [10^6 Pa.K^{-1}]	**$E_{k,H2O}$** [10^8 Pa]
CO_2 (no solvation)	-7.7	6.5	-11.7
CO_2 (solvation)	-7.8	6.5	-11.8
H_2S (no solvation)	-2.5	1.4	-0.99
H_2S (solvation)	0.55	-0.19	2.8
N_2	-11.4	10.3	-17.2
H_2	-8.1	7.8	-11.7
CH_3	-0.04	1.5	-0.83
CH_2	-8.7	6.8	-11.1
CH	-28.0	19.7	-33
C	-41.5	27.5	-46
CH_4	-8.9	8.0	-12.8
C_2H_6	-8.5	7.3	-11.5
CH_{aro}	-6.3	4.6	-7.1
C_{aro}	10.7	-7.2	10.4
$CH_{2,cyclic}$	-8.8	6.9	-10.6
CH_{cyclic} / C_{cyclic}	-4.9	1.9	-0.05
C_2H_4	-5.2	4.9	-8.1
$CH_{2,alkene}$ / CH_{alkene}	-8.9	6.8	-11.1

4.3.3. Addition of Alcohols

Alcohols are present in different industrial processes. Methanol and, to a lesser extent, ethanol are used as hydrate inhibitors during transport. They are often used as solvents in distillation and liquid-liquid extraction. Equilibrium data and predictions are thus necessary for the design and optimisation of processes. In petrochemical industry, they are used as solvents in extractive distillation to separate closely boiling hydrocarbons **[4.9]**. They are also used in the reprocessing of nuclear fuel **[4.10]**. Alcohol-water systems are present in separation of fusel[4] oil from fermentation **[4.11]**. Short chain alcohols are also used as co-emulsifiers in the polymerization of acrylic resins **[4.12]**. They present interesting properties, such as liquidlike density, low viscosity and high diffusivity. For example, the butanol-water system is used in sol-gel processes and after drying in supercritical carbon dioxide, one synthesizes particles with high porosity and large surface area **[4.13]**. In this case, information about carbon-dioxide – water – n-butanol system is required. These few examples give an idea of the multitude of applications of alcohols in the industry and the requirement of accurate phase equilibria predictions, experimental work being too considerable and costly.

Alcohols from methanol to n-decanol have been added to the GC-PR-CPA model. Methanol and ethanol are groups in their own and the others are divided in three groups: $CH_{3,OH}$, $CH_{2,OH}$ and OH.

Initially, adjustments have been made for methanol and ethanol. Then the new groups have been added. First, VLE data of alcohol-alcohol systems have been used to adjust these three new groups between them. Then, it has been extended to the other groups. Bubble pressure calculations (temperatures and liquid compositions are fixed) minimizing the objective function defined by Equation (4.3) have been used to define group parameters for systems with alcohols.

$$\Im = \frac{1}{NEXP}\sum_{i=1}^{NEXP}\left[\frac{P_{i,exp} - P_{i,calc}}{0.01 \times P_{i,exp}}\right]^2 \tag{4.3}$$

Group interaction parameters for methanol are given in Table 4.5, for ethanol in Table 4.6 and for other alcohols in Table 4.7.

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[4] Fusel oil: mixture of several alcohols produced as a by-product of alcoholic fermentation.

Table 4.5: Group interaction parameters for methanol

Groups (k)	C_{kCH3OH} [10^3 Pa.K^{-2}]	D_{kCH3OH} [10^6 Pa.K]	E_{kCH3OH} [10^8 Pa]
CO_2	4.2	-2.6	4.3
N_2	-1.6	1.1	0.039
H_2S	-0.55	0.006	0.18
H_2	2.46	-1.4	4.6
CH_4	1.0	-0.51	1.5
C_2H_6	0.1	5.4	-7.6
CH_3	0.40	0.22	0.0019
CH_2	-0.005	0.044	0.43
CH	-15.5	9.9	-14.4
$CH_{2,cyclic}$	-19.3	12.2	-18.8
CH_{cyclic} / C_{cyclic}	-780	512	-840
CH_{aro}	-50.6	32.05	-51
C_{aro}	25.0	-9.0	3.0
C_2H_4	1.89	-0.77	0.76
CH_{2alk} / CH_{alk}	0.27	0.035	0.20
H_2O	-21.6	15.2	-27

Table 4.6: Group interaction parameters for ethanol

Groups (k)	$C_{kCH3CH2OH}$ [10^3 Pa.K^{-2}]	$D_{kCH3CH2OH}$ [10^6 Pa.K]	$E_{kCH3CH2OH}$ [10^8 Pa]
CO_2	-8.9	5.4	-7.4
N_2	-75	48	-77
H_2	-1.1	0.9	1.1
CH_4	-1.4	0.72	-0.035
C_2H_6	0.1	-0.087	0.59
CH_3	-1.4	0.23	1.0
CH_2	-0.9	0.51	-0.061
CH	94	-61	100
$CH_{2,cyclic}$	1.0	-0.23	0.041
CH_{cyclic} / C_{cyclic}	45.3	-35	67
CH_{aro}	0.92	-0.44	0.52
C_{aro}	-118	83	-147
H_2O	-3.6	3.3	-6.5
CH_3OH	-0.04	-0.011	0.068

Table 4.7: Group interaction parameters for alcohols

Groups	**C** **[10^3 Pa.K^{-2}]**	**D** **[10^6 Pa.K]**	**E** **[10^8 Pa]**
CH_4 + OH	-24.2	-7.6	-2.8
CH_4 + $CH_{3,OH}$	24.0	-6.1	-3.8
CH_4 + $CH_{2,OH}$	1.63	0.29	-2.1
C_2H_4 + OH	5.7	-1.4	-2.3
C_2H_4 + $CH_{3,OH}$	6.4	-5.3	-8.3
C_2H_4 + $CH_{2,OH}$	0.94	-0.48	-3.9
H_2O + OH	-37	-1.8	-19.3
H_2O + $CH_{3,OH}$	47	-13.4	8.5
H_2O + $CH_{2,OH}$	13	-8.8	16.1
CH_3OH + OH	16.3	-8.0	-4.2
CH_3OH + $CH_{3,OH}$	-16.0	-4.7	-8.2
CH_3OH + $CH_{2,OH}$	-0.37	-1.3	4.9
C_2H_5OH + OH	10725	-7794	7196
C_2H_5OH + $CH_{3,OH}$	-190	-10.8	7195
C_2H_5OH + $CH_{2,OH}$	-2621	1939	-3583
OH+$CH_{3,OH}$	-11.6	-15.4	-43
OH+$CH_{2,OH}$	-9.1	-7.1	-7.1
$CH_{3,OH}$ +$CH_{2,OH}$	-7.9	1.3	-8.6

4.4. CONCLUSION

The GC-PR-CPA EoS is a predictive model for systems present in natural gas. The binary interaction parameter defined in the PPR78 model has been modified for binary systems with associating compounds. Group interaction parameters have been adjusted on equilibrium data. Remaning VLE and LLE data are used to validate the model for binary systems (Chapter 5). In the following chapter, the model is also validated for multicomponent systems.

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CHAPTER 5 – VALIDATION OF THE GC-PR-CPA MODEL

L'objectif de ce travail a été de développer un modèle prédictif robuste pour des systèmes comprenant des molécules associative. Le modèle GC-PR-CPA, présenté dans le Chapitre 2, est donc évalué ici pour des systèmes binaires comprenant de l'eau ou des alcools sur des données d'équilibre de la littérature. Pour les systèmes avec l'eau, les solubilités des hydrocarbures, des gaz acides (dioxyde de carbone et sulfure d'hydrogène) et des gaz inertes (azote et hydrogène) ont été considérées. La teneur en eau dans la phase vapeur a été étudiée pour certains systèmes. Quant aux systèmes avec des alcools, les données permettaient de définir des enveloppes de phase complètes. Les résultats sont satisfaisants dans l'ensemble : le modèle reproduit les équilibres de phase ainsi que les comportements spécifiques de certains systèmes, comme les azéotropes. Les déviations sont plus importantes pour les hydrocarbures lourds, étant donné leur faible solubilité et pour la teneur en alcools dans la phase vapeur pour des systèmes avec des gaz légers (méthane, éthane ou dioxyde de carbone).

Les capacités prédictives du modèle GC-PR-CPA sont évaluées sur des données d'équilibres liquide-vapeur de la littérature pour des systèmes multi-constituants comprenant de l'eau et/ou des alcools. Les résultats sont satisfaisants en général. Le modèle est aussi utilisé pour prédire les courbes de dissociation d'hydrates de certains systèmes présentés dans le chapitre 3. Il est montré que le modèle est en accord avec les données expérimentales pour des systèmes sans inhibiteurs et avec du méthanol mais présente des écarts pour les mélanges de l'éthanol. Ceci est principalement du aux déviations observées dans la prédiction des diagrammes de phases. Enfin, outre les équilibres entre phases, les grandeurs de mélange, nécessaires dans le cadre de la conception de procédés sont prédits avec plus ou moins de précision. Le modèle a été développé à partir de données d'équilibres uniquement.

5.1 INTRODUCTION

The objective of this work is to develop a reliable predictive model for systems containing associative compounds. Group parameters have been defined for water and alcohols with hydrocarbons, acid and inert gases in Chapter 4. Results for binary systems with water, methanol and ethanol, and to a lesser extent, other alcohols are presented in this chapter, using the data listed in Appendices A1 to 18. For binary systems with water, the model has been evaluated on its ability to predict solubility either for VLE or LLE. Water content has also been considered for some systems. Tsonoupoulos published a correlation for hydrocarbons – water mutual solubilities **[5.1, 5.2]**. This correlation is in good agreement with experimental data and therefore has been compared to the GC-PR-CPA model. For binary systems with alcohols, entire phase diagrams were available, so predictions were made for both phases.

The model is considered accurate if it is close to experimental data within the experimental error, which represents a kind of confidence interval. If the experimental error is given by the authors in their publications, it is reported in tables (EE for Experimental Error). In the case of several values, the maximum error is reported. If it is not specified, it is set arbitrarily to 5%.

Systems of interest contain more than two compounds. The model is then evaluated for multicomponent systems. Its ability to predict hydrate stability zone is also considered in the second part, for some mixtures presented in Chapter 2. Finally, since mixing enthalpies are involved in the energy balances, the accuracy of the model to predict such derivate property is checked. In these three parts, systems have been chosen to show the model accuracy and its limits.

As for binary systems, if the experimental error (EE) is given by the authors, it is reported here; otherwise it is set to 5%. For hydrate stability zone, an error bar of 0.5 K is preferred to the uncertainties calculated in Appendix E, to have a constant value for a better visibility. In process design, the maximum deviation usually accepted between predicted and experimental mixing enthalpies is 10%.

5.2. BINARY SYSTEMS WITH WATER

5.2.1. Correlation for Hydrocarbons – Water Systems

The correlations defined by Tsonopoulos **[5.1, 5.2]** for hydrocarbons solubilities in water and vice-versa are valid for isobaric systems. Since water content data have been evaluated for isothermal systems, only the correlation for hydrocarbons solubilities in water is presented.

The development of the correlation is based on the relation between the heat of solution and the solubility of hydrocarbons in water (Equation (5.1)) **[5.1]**:

$$\left(\frac{\partial ln(x_i)}{\partial T}\right)_P \cong \frac{\Delta \bar{h_\iota}}{RT^2} \tag{5.1}$$

where x_i is the solubility of the component *i* and h_i is the heat of solution.

Gill et al. **[5.3, 5.4]** established that the heat of solution is a linear function of temperature. Thus, by integrating Equation (5.1), one obtains an expression relating hydrocarbons solubility in water and the temperature (Equation (5.2)).

$$ln(x_i) = \mathcal{A}_i + \frac{\mathcal{B}_i}{T} + \mathcal{C}_i ln(T) \tag{5.2}$$

Alkanes, naphthenic and aromatic hydrocarbons show an isobaric minimum of solubility. From Equation (5.2), the temperature of the minimum of solubility is defined by:

$$T_{min,i} = \frac{\mathcal{B}_i}{\mathcal{C}_i} \tag{5.3}$$

Equation (5.2) has been compared to the GC-PR-CPA model for normal alkanes (from C_5), naphthenic and aromatic hydrocarbons.

5.2.2. Normal Alkanes

Natural gases are mostly composed of light hydrocarbons with traces of heavier hydrocarbons. Normal alkanes – water binary systems from methane to *n*-eicosane have been considered. Absolute errors and Average Absolute Deviations (AAD) between experimental data and the GC-PR-CPA model are presented in Table 5.1.

Table 5.1: Deviations between the GC-PR-CPA model and experimental data for normal alkanes – water binary systems

Groups	Compounds	Absolute Error [mole fraction]		AAD [%]	EE [%]	Temperature range [K]	Pressure range [MPa]
		Min	Max				
CH_4	Methane	$7.2.10^{-8}$	$1.7.10^{-2}$	6	5	274 – 623	0.1 – 108
C_2H_6	Ethane	$9.9.10^{-9}$	$3.6.10^{-3}$	7	7	259 – 444	0.05 – 685
CH_3, CH_2	Propane	$3.0.10^{-8}$	$1.4.10^{-4}$	17		247 – 422	0.01 – 19
	n-Butane	$4.7.10^{-8}$	$3.1.10^{-4}$	12		273 – 511	0.1 – 69
	n-Pentane	$6.9.10^{-8}$	$1.8.10^{-2}$	17		273 – 603	0.02 – 71
	n-Hexane	$4.4.10^{-8}$	$2.3.10^{-6}$	12		273 – 425	0.01 – 0.8
	n-Heptane	$5.5.10^{-9}$	$6.7.10^{-7}$	17		273 – 444	0.1
	n-Octane	$9.9.10^{-9}$	$3.6.10^{-3}$	35		273 – 456	0.1
	n-Nonane	$6.3.10^{-10}$	$3.9.10^{-7}$	38		288 – 410	0.1
	n-Decane	$1.8.10^{-10}$	$4.9.10^{-9}$	36		293 – 298	0.1
	n-Undecane	$1.0.10^{-10}$	$2.0.10^{-10}$	32		298	0.1
	n-Dodecane	$3.4.10^{-10}$	$7.5.10^{-8}$	91	16	298 – 423	0.1 – 5
	n-Tetradecane	$2.0.10^{-10}$	$1.3.10^{-7}$	93		298 – 473	0.1 - 5
	n-Hexadecane	$7.0.10^{-11}$	$4.4.10^{-8}$	99		298 – 526	0.1 – 5
	n-Octadecane	$5.0.10^{-11}$	$5.0.10^{-11}$	34		298	0.1
	n-Eicosane	$1.0.10^{-11}$	$4.0.10^{-9}$	64		298 – 473	0.1 - 5

The GC-PR-CPA model is in good agreement with experimental data for light alkanes within experimental error (see Figure 5.1). However, alkanes from *n*-octane have low solubility in water (lower than 10^{-8} mole fraction) and the model is not able to represent accurately the behaviour of these alkanes from *n*-octane. Furthermore, limited data are available for these compounds and it is difficult to evaluate the quality of experimental data. Finally, it is stated that Peng-Robinson EoS, as all cubic equations of state with two parameters (attractive parameter *a* and co-volume *b*), is poorly accurate for high boiling hydrocarbons and would also explain the larger deviations. Indeed, in liquid state, molecules are closer to each other than in gas state. Parameter *b* represents the volume of molecules and is more effective in liquid densities calculations. Therefore, it is more important than the parameter *a* in liquid state calculations. But this parameter is kept constant **[5.5]**.

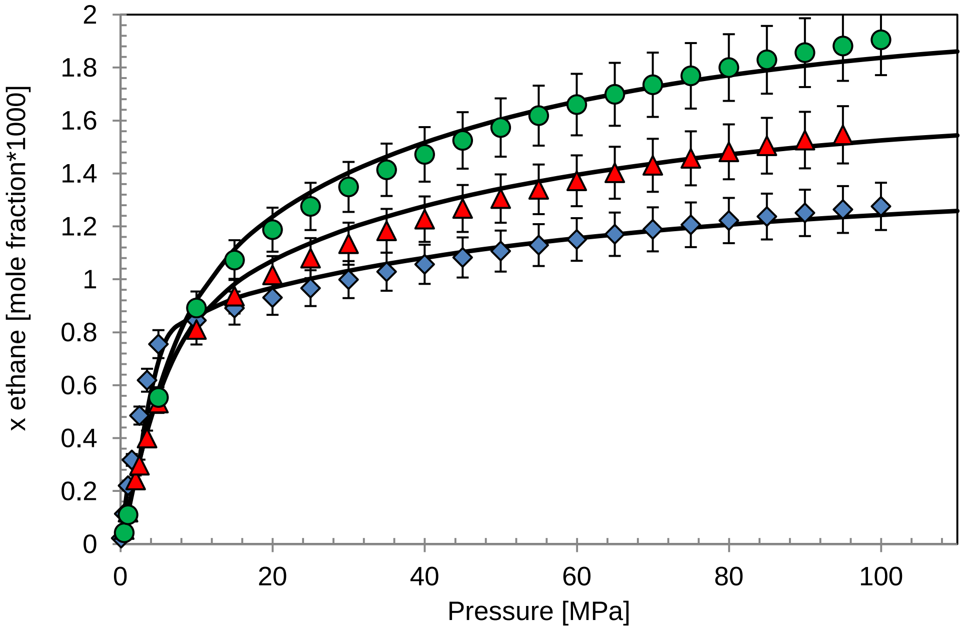

Figure 5.1: Ethane solubility in water at 313.15 K (♦), 373.15 K (▲) and 393.15 K (●) **[5.6]**. *(-) GC-PR-CPA model. Error bar: ± 7%*

It has also to be mentioned, that the GC-PR-CPA model has been adjusted on solubility data of selected alkanes and its parameters have been validated for the remaining ones. Therefore the model cannot be completely accurate. However for alkanes from *n*-propane to *n*-hexane, the accuracy is globally acceptable with better representation for alkanes with an even number of carbon. There could be an "odd-even" effect.

Since Tsonopoulos correlation is able to well represent alkanes solubility in water, it is compared to the GC-PR-CPA model for two systems: *n*-pentane – water and *n*-hexane – water (see Figure 5.2).

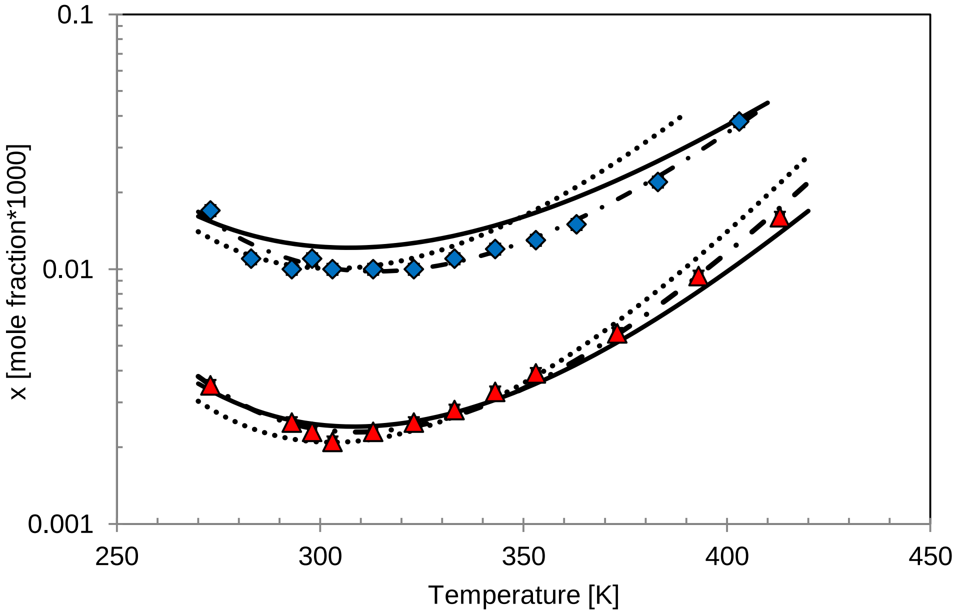

Figure 5.2: n-pentane (♦) **[5.7]** *and n-hexane (▲)* **[5.8]** *solubilities in water at atmospheric pressure. (-) GC-PR-CPA model. (……) Tsonopoulos correlation. (▬ ▪) Readjusted Tsonopoulos correlation. Error bar: ± 5%*

Parameters of Equation (5.2) have also been readjusted on literature data presented on Figure 5.2 (Table 5.2).

Table 5.2: n-Pentane and n-hexane solubility in water with Equation (5.2)

Compounds	**Correlation**	$\mathcal{A}$ **[-]**	$\mathcal{B}$ **[K]**	$\mathcal{C}$ **[-]**	T_{min} **[K]**
***n*-Pentane**	Tsonopoulos **[5.2]**	-333.60	14537.47	47.97	303.03
	Readjusted	-320.37	14351.21	45.77	313.57
***n*-Hexane**	Tsonopoulos **[5.2]**	-374.91	16327.13	53.90	302.94
	Readjusted	-368.81	16327.25	52.85	308.96

As seen on Figure 5.2, the GC-PR-CPA model presents some deviation with experimental data selected for the *n*-pentane – water system with 21% of deviation, but is in good agreement for the *n*-hexane – water system (7%). For both systems, it is able to represent the minimum of solubility. The temperature of minimum of solubility for the *n*-pentane – water system is 315.40 K, which is close to the one obtained with readjusted parameters. It is 305.39 K for the *n*-hexane – water system.

Correlation with readjusted parameters is clearly the better representation of alkanes solubility with only 5% and 4% of deviation. For the *n*-pentane – water system, the original version of Equation (5.2) presents 18% of deviation, which is better than the GC-PR-CPA model, but 11% for the *n*-hexane – water system. It can be explained by the difference of data used for the parameters fitting.

The ability of the model to predict water content is also evaluated here. Water content in light hydrocarbons is in good agreement with experimental data, considering the experimental error (e.g. methane – water **[5.9]** and ethane – water on Figure 5.3).

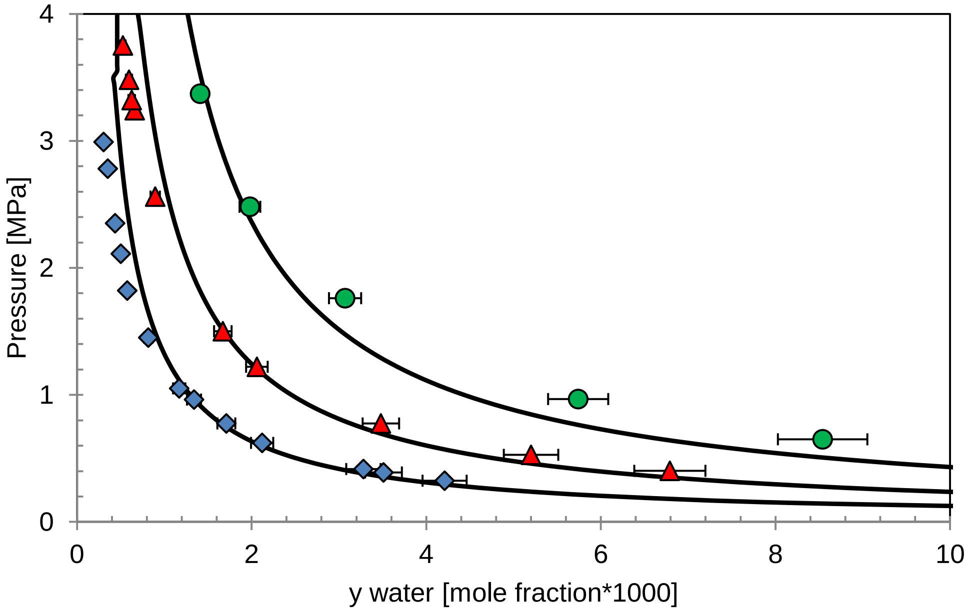

Figure 5.3: Water content in ethane at 283.11 K (♦), 293.11 K (▲) and 303.15 K (●) **[5.10]**. *(-) GC-PR-CPA model. Error bar: ± 6%*

However, as seen in Figure 5.4, the model fails to predict water solubility in heavier alkanes. Lower deviations are about 38%. And highest deviations are at lower temperatures. But the model is, at least, able to reproduce the right shape of water solubility in alkanes.

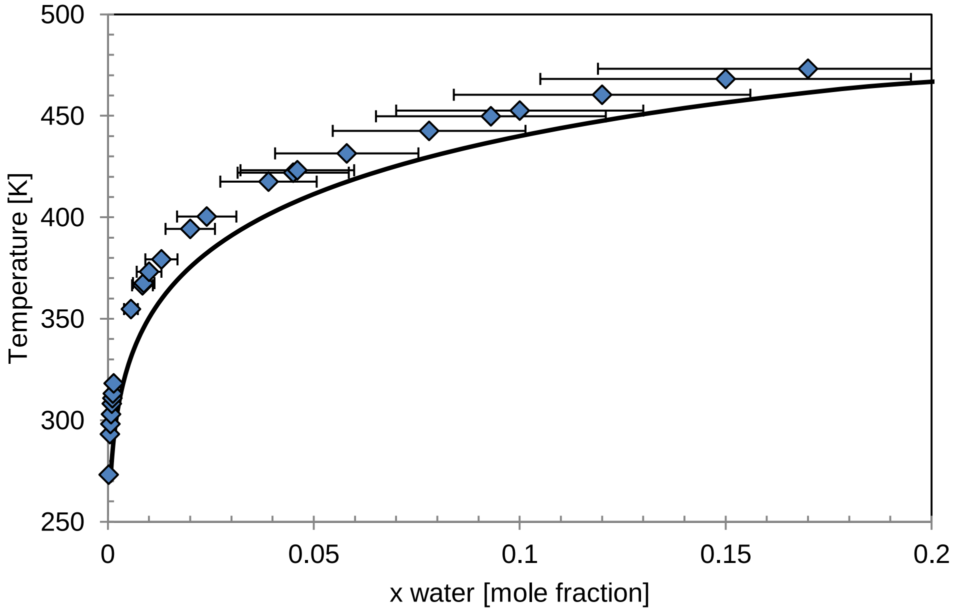

Figure 5.4: Water solubility in n-hexane at atmospheric pressure (♦) **[5.8]**. *(-) GC-PR-CPA model. Error bar from* **[5.8]**: *± 30%*

As explained before, LLE for heavier hydrocarbons are poorly predicted and it has been shown that water solubility predictions present even more deviations. A solution would be to change the expression of the co-volume *b*, by introducing a mixing rule as for the attractive parameter *a*, with a binary interaction parameter l_{ij}.

5.2.3. Branched Alkanes

Branched alkanes have also been included in the GC-PR-CPA model. Limited data are available for these compounds and for limited range of pressure. As seen in Table 5.3, the model is better in VLE predictions (*i*-butane – water system) than for LLE.

Table 5.3: Deviations between the GC-PR-CPA model and experimental data for branched alkanes – water binary systems

Groups	**Compounds**	**Absolute Error [mole fraction]**		**AAD[%]**	**Temperature range [K]**	**Pressure range [MPa]**
		Min	**Max**			
CH_3, CH_2, CH	*i*-Butane	$5.5.10^{-8}$	$1.7.10^{-6}$	5	278 – 318	0.1
	i-Pentane	$3.6.10^{-7}$	$4.4.10^{-6}$	23	273 – 333	0.1

Table 5.3 (to be continued): Deviations between the GC-PR-CPA model and experimental data for branched alkanes – water binary systems

Groups	Compounds	Absolute Error [mole fraction]		AAD[%]	Temperature range [K]	Pressure range [MPa]
		Min	Max			
CH_3, CH_2, CH	*2,3-*Dimethylbutane	$4.3.10^{-8}$	$5.0.10^{-6}$	20	273 – 423	0.1 – 0.7
CH_3, CH_2, C	*2,2-*Dimethylpropane	$1.8.10^{-6}$	$1.8.10^{-6}$	22	298	0.1
	*2,2-*Dimethylbutane	$2.5.10^{-7}$	$1.4.10^{-6}$	17	273 – 298	0.1
	*2,2-*Dimethylpentane	$2.5.10^{-7}$	$2.5.10^{-7}$	32	298	0.1
	*3,3-*Dimethylpentane	$1.8.10^{-8}$	$9.6.10^{-7}$	16	298 – 423	0.1

5.2.4. Alkenes

Two alkenes have been added to the GC-PR-CPA model: ethylene and propylene.

Table 5.4: Deviations between the GC-PR-CPA model and experimental data for alkenes – water binary systems

Groups	Compounds	Absolute Error [mole fraction]		AAD [%]	EE [%]	Temperature range[K]	Pressure range [MPa]
		Min	Max				
C_2H_4	Ethylene	$2.2.10^{-19}$	$4.6.10^{-4}$	7	-	298 – 394	0.1 – 53
$CH_{2,alk}$ / CH_{alk}	Propylene	$3.2.10^{-7}$	$3.7.10^{-4}$	8.5	4	311 – 411	0.15 – 32

As seen in Table 5.4, the model is in good agreement with experimental data, except deviations up to 25% at higher pressures and temperatures (see Figure 5.5).

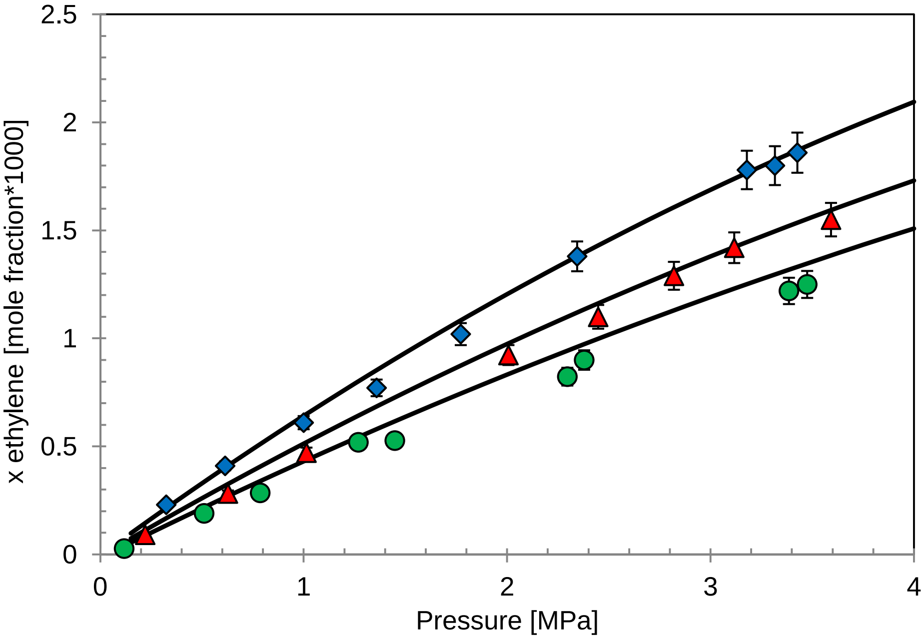

Figure 5.5: Ethylene solubility in water at 310.93 K (♦), 327.59 K (▲) and 344.26 K (●) **[5.11]**. *(-) GC-PR-CPA model. Error bar: ± 5%*

5.2.5. Naphthenic Hydrocarbons

The GC-PR-CPA model has been extended to naphthenic (or cyclic) hydrocarbons. Comparison between the model and experimental data is limited to five compounds due to availability of data in the literature.

Table 5.5 gives the deviations from experimental data. Considering that the model is less accurate for LLE and the low solubility in water, the model is in good agreement with experimental data for cyclohexane, methylcyclopentane and methylcyclohexane.

As shown on Figure 5.6, the model describes well the cyclohexane behaviour. However, it fails to describe minimum of solubility of methylcyclohexane in water with temperature. It shows also higher discrepancies for cyclopentane and cycloheptane. There is only one data set point for cycloheptane, therefore the results have to been taken carefully. For cyclopentane, the model reproduces the behaviour but over predicts the solubility.

Table 5.5: Deviations between the GC-PR-CPA model and experimental data for naphthenic hydrocarbons – water binary systems

Groups	**Compounds**	**Absolute Error [mole fraction]**		**AAD [%]**	**Temperature range [K]**	**Pressure range [MPa]**
		Min	**Max**			
$CH_{2,cyclic}$	Cyclopentane	$1.9.10^{-5}$	$5.0.10^{-5}$	52	278 – 373	0.1
	Cyclohexane	$1.9.10^{-7}$	$7.6.10^{-6}$	13	274 – 425	0.1
	Cycloheptane	$2.3.10^{-6}$	$2.3.10^{-6}$	41	298	0.1
$CH_{2,cyclic}$, CH_{cyclic} / C_{cyclic}	Methyl-cyclopentane	$1.5.10^{-8}$	$5.2.10^{-4}$	24	298 – 487	0.1
	Methyl-cyclohexane	$3.3.10^{-7}$	$1.8.10^{-6}$	22	298 – 423	0.1

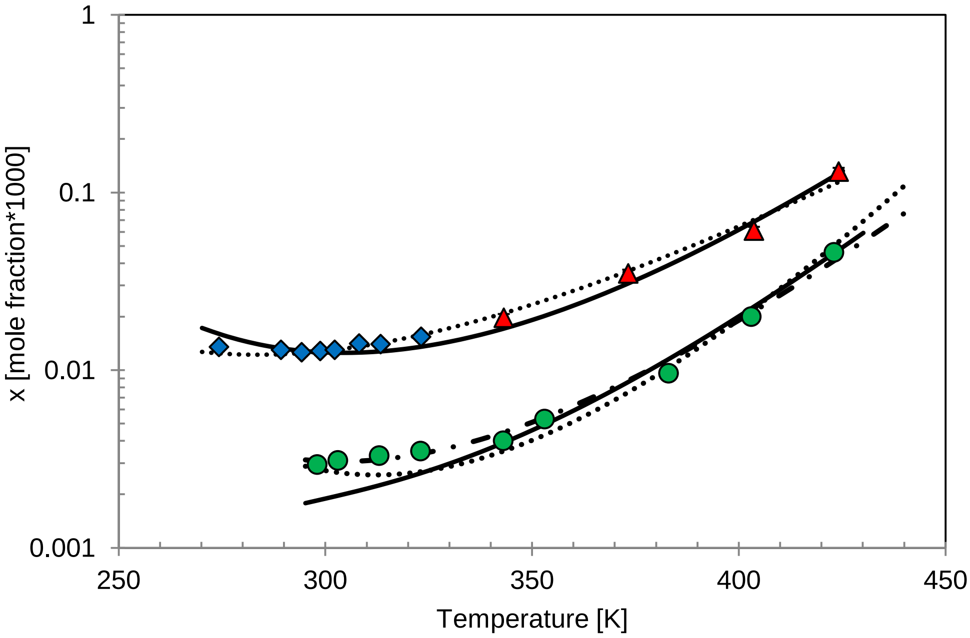

Figure 5.6: Cyclohexane (♦) **[5.12]** *and (▲)* **[5.13]**, *and Methylcyclohexane (●)* **[5.14]** *solubilities in water at atmospheric pressure. (-) GC-PR-CPA model. (……) Tsonopoulos correlation. (▬ ▪) Readjusted Tsonopoulos correlation. Error bar: ± 5%*

Parameters for cyclohexane and methylcyclohexane determined by Tsonopoulos are given in Table 5.6. These parameters have also been fitted to the experimental data presented in Figure 5.6. The same parameters have been obtained for cyclohexane. But the fitting of parameters for the system methylcyclohexane – water improved the correlation.

Table 5.6: Cyclohexane and methylcyclohexane solubility in water with Equation (5.2)

Compounds	Correlation	$\mathcal{A}$ [-]	$\mathcal{B}$ [K]	$\mathcal{C}$ [-]	T_{min} [K]
Cyclohexane	Tsonopoulos **[5.2]**	-219.86	8893.78	31.37	283.47
Methylcyclohexane	Tsonopoulos **[5.2]**	-491.07	22132.10	70.92	312.09
	Readjustment	-366.03	15971.10	52.61	303.55

The correlation presents a deviation of 5% for the systems cyclohexane – water, while the model deviates from 8%. There GC-PR-CPA model predicts a minimum of solubility at 297.78 K, which is higher than the one given by Equation (5.3). Deviations for the methylcyclohexane – water system are 20% for the GC-PR-CPA model, 14% for the original version of Equation (5.2) and 7% for the readjusted one.

5.2.6. Aromatic Hydrocarbons

The GC-PR-CPA model is able to predict benzene, toluene, ethylbenzene and xylenes solubility in water. Deviations from experimental data are presented in Table 5.7.

Table 5.7: Deviations between the GC-PR-CPA model and experimental data for aromatic hydrocarbons – water binary systems

Groups	Compounds	Absolute Error [mole fraction]		AAD [%]	EE [%]	Temperature range [K]	Pressure range [MPa]
		Min	Max				
CH_{aro}	Benzene	$4.0.10^{-8}$	$8.5.10^{-4}$	5	7	260 – 572	0.1 – 81
CH_{aro}, C_{aro}	Toluene	$2.3.10^{-7}$	$4.1.10^{-5}$	7	10	273 – 583	0.1 – 61
	Ethylbenzene	$2.1.10^{-7}$	$1.8.10^{-5}$	13		273 – 393	0.1 – 7
	m-Xylene	$5.5.10^{-7}$	$1.7.10^{-5}$	17		273 – 318	0.1
	o-Xylene	$1.6.10^{-7}$	$7.3.10^{-6}$	15		273 – 343	0.1
	p-Xylene	$1.1.10^{-6}$	$2.1.10^{-5}$	21		273 - 363	0.1

The model is in good agreement with experimental data, especially for benzene and toluene. It under predicts ethylbenzene solubility in water, but is still in the confidence interval of the experimental error. Data for xylenes are scattered. But in general, the model seems to under predict *p*-xylene solubility and over predict for the two others. Equation (5.2) is also valid for aromatic hydrocarbons. Preliminary results have been published **[5.9]**. However, to improve the model, parameters of the GC-PR-CPA EoS have been readjusted as well as the parameters of Equation (5.2) to the data presented on Figure 5.7 and Figure ***5.8***. Parameters given by Tsonopoulos **[5.2]** and the ones readjusted are presented in Table 5.8.

Table 5.8: Benzene, toluene and ethylbenzene solubility in water with Equation (5.2)

Compounds	**Correlation**	$\mathcal{A}$ **[-]**	$\mathcal{B}$ **[K]**	$\mathcal{C}$ **[-]**	**T_{min} [K]**
Benzene	Tsonopoulos **[5.2]**	-192.48	8053.11	27.67	290.99
	Readjustment	-171.09	6999.75	24.54	285.27
Toluene	Tsonopoulos **[5.2]**	-221.74	9274.79	31.87	291.00
	Readjustment	-221.74	9274.79	31.86	291.08
Ethylbenzene	Tsonopoulos **[5.2]**	-263.22	11024.75	37.89	291.00
	Readjustment	-261.26	11021.60	37.54	293.56

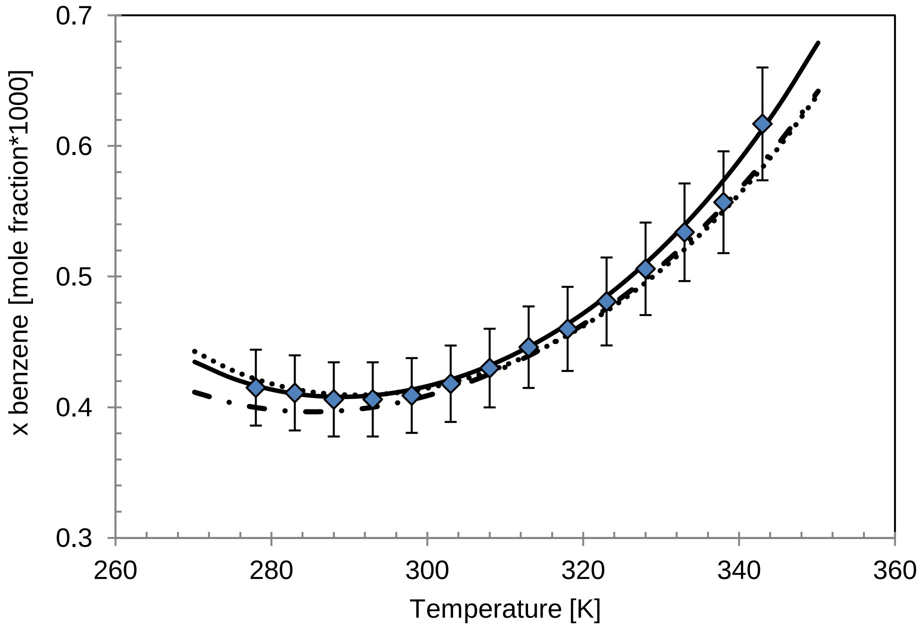

Figure 5.7: Benzene solubility in water at atmospheric pressure (♦) **[5.15]**. *(-) GC-PR-CPA model. (…..) Tsonopoulos correlation. (▬ ▪) Readjusted Tsonopoulos correlation. Error bar: ± 7%*

Deviations from these experimental data are 3% for the GC-PR-CPA model and 2% for the correlation with both sets of parameters.

The temperature of the minimum of solubility predicted by the GC-PR-CPA model is 290.12 K, close to the one given by Tsonopoulos (see Table 5.8) and Bohon and Claussen (291.15 K) **[5.16]**. A seen on Figure 5.7, the readjusted correlation represents well the solubility at higher temperatures, but does not reproduce accurately the minimum of solubility, explaining the lower predicted temperature.

Figure 5.8 compares experimental solubility of toluene and ethylbenzene in water with the GC-PR-CPA model and correlations.

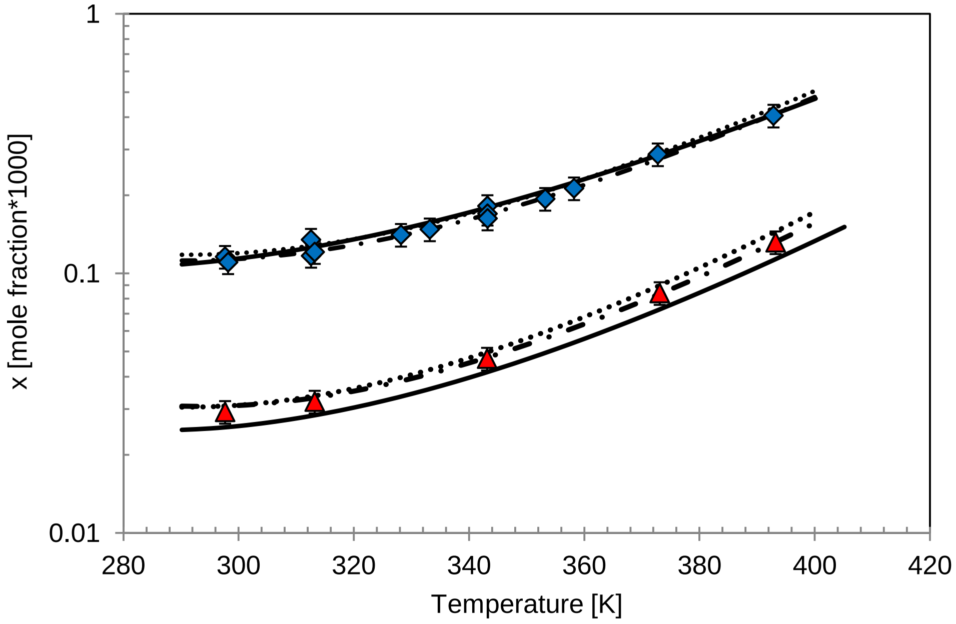

Figure 5.8: Toluene (♦) and Ethylbenzene (▲) solubilities in water at 0.5 MPa **[5.17]**. *(-) GC-PR-CPA model. (……) Tsonopoulos correlation. (▬ ▪) Readjusted Tsonopoulos correlation. Error bar: ± 10%*

The GC-PR-CPA model deviates from 5% and 12% for the toluene – water system and the toluene –water system, repectively. The original equation (5.2) deviates respectively from 5 % and 7%, while the readjusted one presents deviations of 3% and 2%.

Bohon and Claussen **[5.16]** measured a temperature of the minimum of solubility of 291.15 K for aromatic hydrocarbons. The temperature predicted by the GC-PR-CPA model is 292.08 K for the toluene – water system and 291.32 K for the ethylbenzene – water system, which is close to the experimental measurements. Even if the model under predicts the solubility for the ethylbenzene – water system, the temperature of the minimum of solubility is well determined.

5.2.7. Gases

In this part, predictions for acid (CO_2 and H_2S) and inert (N_2 and H_2) gases are presented. Deviations from experimental data are given in Table 5.9.

Table 5.9: Deviations between the GC-PR-CPA model and experimental data for acid gases – water and inert gases – water binary systems

Groups	**Compounds**	**Absolute Error [mole fraction]**		**AAD [%]**	**EE [%]**	**Temperature range [K]**	**Pressure range [MPa]**
		Min	**Max**				
CO_2	Carbon dioxide (solvation)	$7.1.10^{-8}$	$4.1.10^{-2}$	7	7	273 – 607	0.008 – 80
	Carbon dioxide (no solvation)	$9.6.10^{-7}$	$9.6.10^{-3}$	8			
H_2S	Hydrogen sulphide (solvation)	0	$1.8.10^{-2}$	7	7	273 – 594	0.04 – 21
	Hydrogen sulphide (no solvation)	0	$8.4.10^{-3}$	10			
N_2	Nitrogen	$4.0.10^{-7}$	$3.4.10^{-4}$	9	2.5	273 – 589	0.1 – 61
H_2	Hydrogen	$1.5.10^{-7}$	$3.5.10^{-3}$	7	10	273 – 423	0.1 – 101

In general, the GC-PR-CPA model is in good agreement with experimental data. Deviations are more important at low temperatures and high pressures, but still accurate within the experimental error.

The model took also into account the solvation of carbon dioxide and hydrogen sulphide in water. A comparison is done for these systems between predictions taking into solvation and without solvation (Figure 5.9 and Figure ***5.10***). For hydrogen sulphide, solvation is clearly improving predictions. For carbon dioxide, it improves predictions at higher temperatures, but presents some discrepancies at lower ones, still acceptable considering the experimental error.

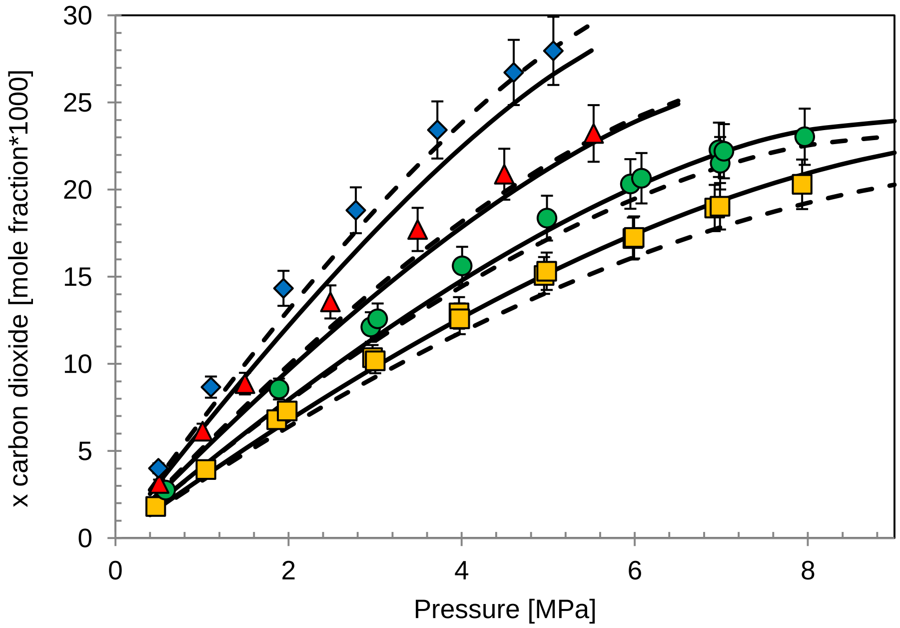

Figure 5.9: Carbon dioxide solubility in water at 288.26 K (♦), 298.28 K (▲), 308.2 K (●) and 318.23 K (■) **[5.18]**. *(-) GC-PR-CPA model + solvation. (- -) GC-PR-CPA without solvation. Error bar: ± 7%*

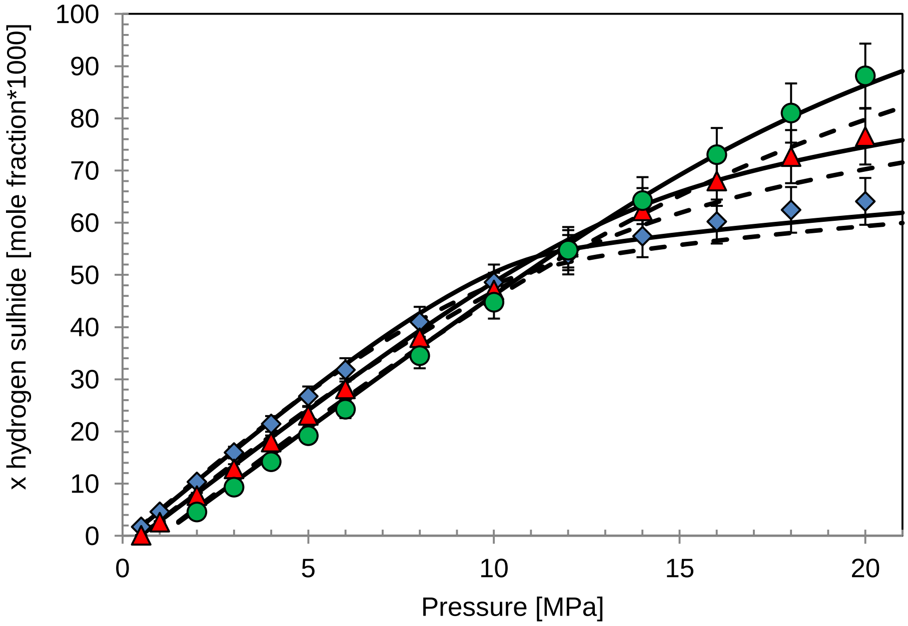

Figure 5.10: Hydrogen sulphide solubility in water at 393.15 K (♦), 423.15 K (▲) and 453.15 K (●) **[5.19]**. *(-) GC-PR-CPA model + solvation. (- -) GC-PR-CPA without solvation. Error bar: ± 5%*

The GC-PR-CPA is also able to predict accurately water content in gases, within the experimental error. The example of water content in carbon dioxide at four temperatures is shown on Figure 5.11. Deviations are about 6% for these data.

Predictions with and without solvation are similar at lower pressures. However, there is a difference at high pressures (see Figure 5.12). In this case, taking into account solvation improves predictions and the behaviour is better reproduced.

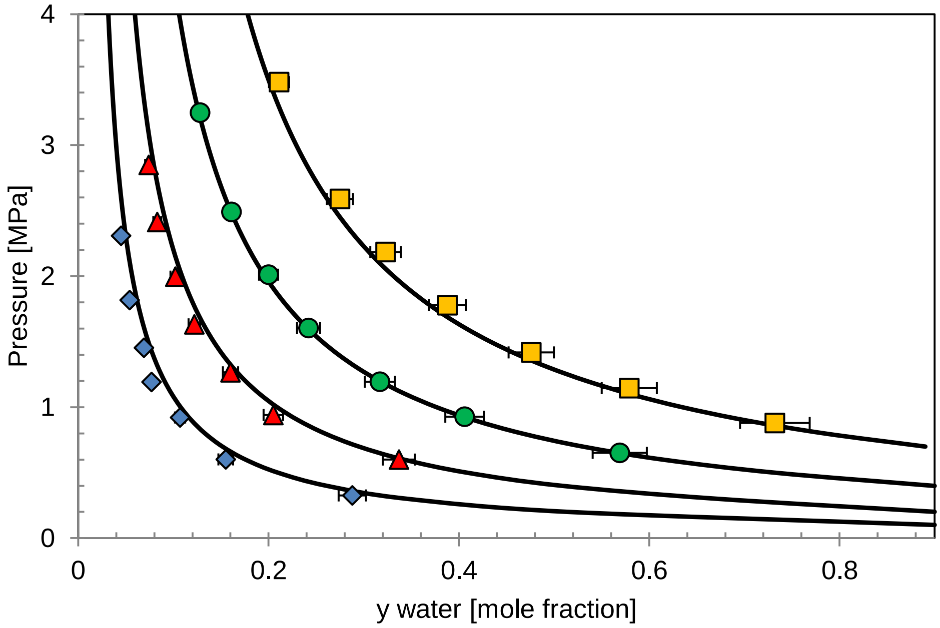

Figure 5.11: Water content in carbon dioxide at 373.15 K (♦), 393.15 K (▲), 413.15 K (●) and 433.15 K (■) **[5.20]**. *(-) GC-PR-CPA model. Error bar: ± 5%*

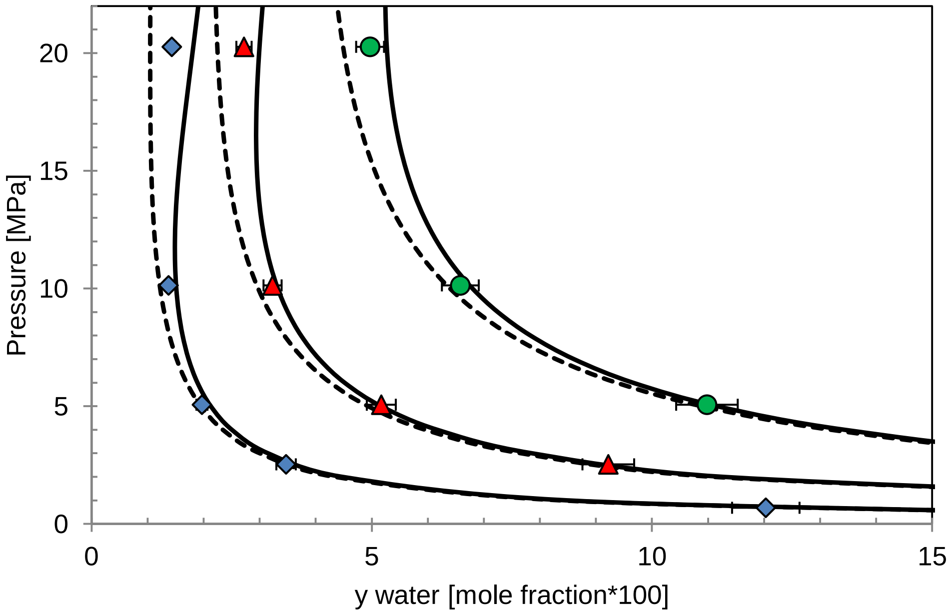

Figure 5.12: Water content in carbon dioxide at 366.48 K (♦),394.26 K (▲) and 422.04 K (●) **[5.21]**. *(-) GC-PR-CPA model + solvation. (- -) GC-PR-CPA without solvation. Error bar: ± 5%*

5.2.8. Alcohols

The model has been extended to alcohols. Deviations for water – methanol and water – ethanol systems are given in Table 5.10.

Table 5.10: Deviations between the GC-PR-CPA model and experimental data for alcohol – water binary systems

Groups	**Compounds**	**AAD [%]**			**Temperature range [K]**	**Pressure range [MPa]**
		P	**y**	**y alcohol**		
CH_3OH	Methanol	2	5	5	308 – 442	0.006 – 2
C_2H_5OH	Ethanol	7	7	10	283 – 548	0.002 – 10
$CH_{3,OH}$, $CH_{2,OH}$, OH	*n*-Propanol	5	10	15	273 – 373	7.10^{-4} – 0.1
	n-Butanol	10	12	24	298 – 444	9.10^{-4} – 0.5
	n-Hexanol	9	1	30	294 – 430	1.10^{-4} – 0.1

The GC-PR-CPA model is in good agreement with experimental data for systems with methanol and ethanol. It is able to represent the alcohols solubility in water but also the alcohol and the water content. As seen on Figure 5.13, the water – ethanol system presents an azeotrope. The model predicts an azeotrope but at higher ethanol molar fractions.

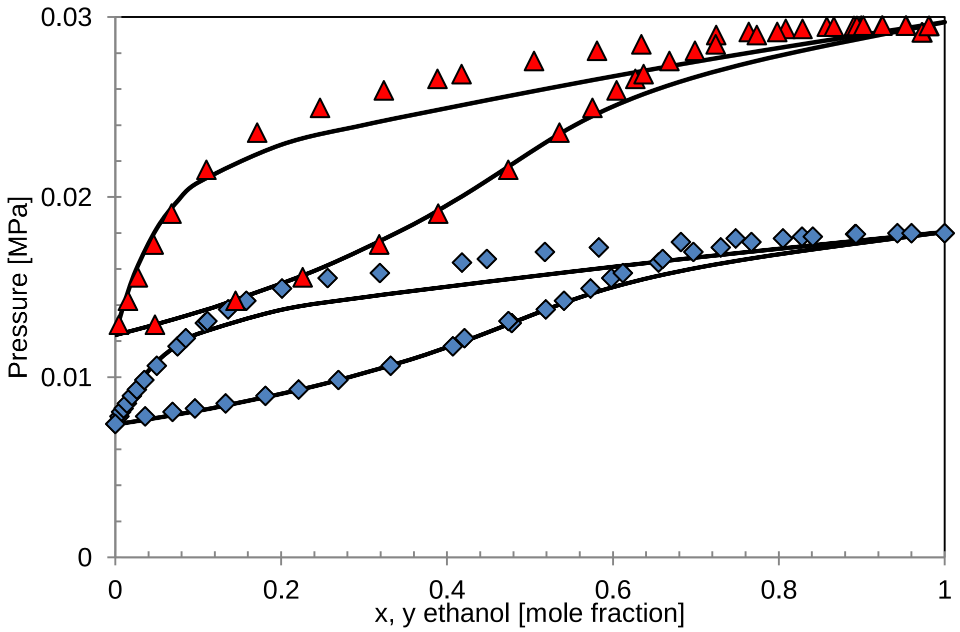

Figure 5.13: Phase equilibria of the binary system water – ethanol at 313.15 K (♦) **[5.22]** *and 323.15 K (▲)* **[5.23]**. *(-) GC-PR-CPA model. Error bar: ± 5%*

For systems with other alcohols, the model presents some deviations with experimental data, especially for the vapour phase.

Freezing points have been taken into account for methanol – water and ethanol – water binary systems. The model is able to predict freezing points with an accuracy of 1.1% for the methanol – water system and 1.4% for the ethanol – water system.

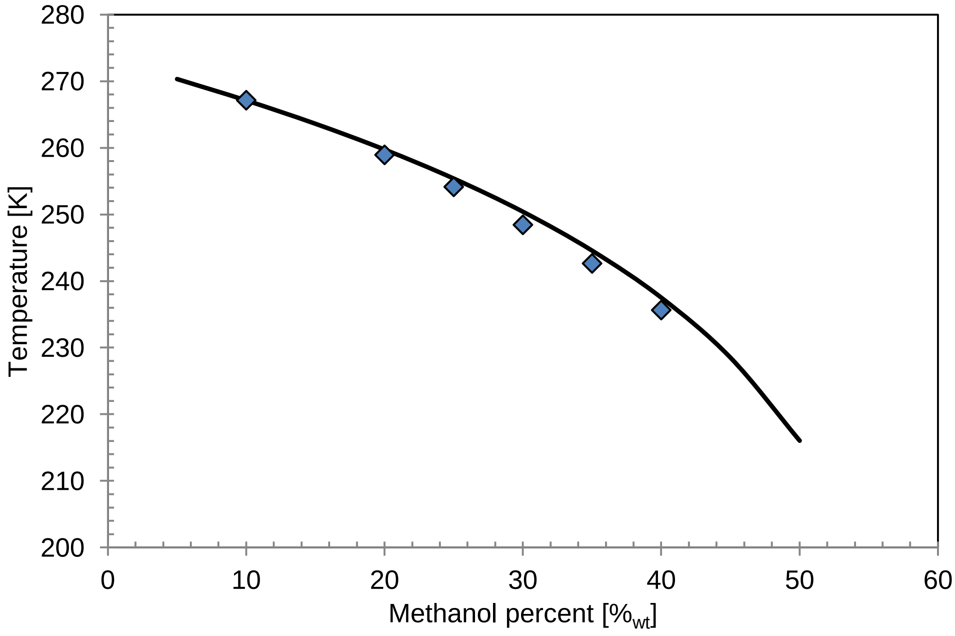

Figure 5.14: Freezing points of the binary system water – methanol at 313.15 K **[5.24]**. *(-) GC-PR-CPA model.*

5.3. BINARY SYSTEMS WITH METHANOL

To predict hydrate stability zone with methanol as an inhibitor, it is first important to well represent it with the other compounds present. In this part, the results for binary systems of hydrocarbons or single gases with methanol are presented.

5.3.1. Normal Alkanes

As for water, binary systems normal alkanes – methanol have been considered. Group parameters have been determined for methane – methanol system using flash calculations, while bubble point calculations have been employed for the others. That is why, deviations with experimental data are given either on solubility or on pressure.

Table 5.11: Deviations between the GC-PR-CPA model and experimental data for methane – methanol binary system

Group	**Compound**	**AAD [%]**			**Temperature range [K]**	**Pressure range [MPa]**
		x methane	**y methane**	**y methanol**		
CH_4	Methane	8	1.3	23	183 – 472	0.1 – 250

Table 5.12: Deviations between the GC-PR-CPA model and experimental data for normal alkanes – methanol binary system

Groups	**Compounds**	**AAD [%]**			**Temperature range [K]**	**Pressure range [MPa]**
		P	**y**	**y methanol**		
C_2H_6	Ethane	12	0.1	7	184 – 373	0.06 – 7
CH_3, CH_2	Propane	6	4	14	293 – 474	0.06 – 9
	n-Butane	4	7	8	264 – 470	0.06 – 140
	n-Pentane	3	4	7	270 – 423	0.05 – 140
	n-Hexane	7	6	7	255 – 513	0.02 – 151
	n-Heptane	9	11	3	268 – 540	0.01 – 151

Table 5.12 (to be continued): Deviations between the GC-PR-CPA model and experimental data for normal alkanes – methanol binary system

Groups	Compounds	AAD [%]			Temperature range [K]	Pressure range [MPa]
		P	y	y methanol		
CH_3, CH_2	*n*-Nonane	4	-	-	416 – 537	1 – 8
	n-Decane	3	-	-	422 – 540	1 – 8
	n-Dodecane	3	-	-	278 – 536	0.1 – 9
	n-Tetradecane	2.5	-	-	298 – 535	0.1 – 9
	n-Hexadecane	5	-	-	298 – 318	5.10^{-4} – 0.04

As seen in Table 5.11 and Table ***5.12***, the model is in good agreement with experimental data. However, it presents some discrepancies for methanol content in light hydrocarbons. Despite many different adjustments, using flash or bubble point calculations with different data, the results have not been improved.

5.3.2. Branched Alkanes

Bubble point calculations have been applied to determine the parameters for branched alkanes – methanol systems. Deviations are presented in Table 5.13.

Table 5.13: Deviations between the GC-PR-CPA model and experimental data for branched alkanes – methanol binary systems

Groups	Compounds	AAD [%]			Temperature range [K]	Pressure range [MPa]
		P	y	y methanol		
CH_3, CH_2, CH	*i*-Butane	5.5	3	18	273 – 423	0.03 – 5
	i-Pentane	2	2	11	297 – 305	0.1
	2,3-Dimethylbutane	3	3	6	283 – 334	0.1

As for normal alkanes, the methanol content is better described for heavier hydrocarbons, but it is able to represent the shape of the phase equilibrium (see Figure 5.15).

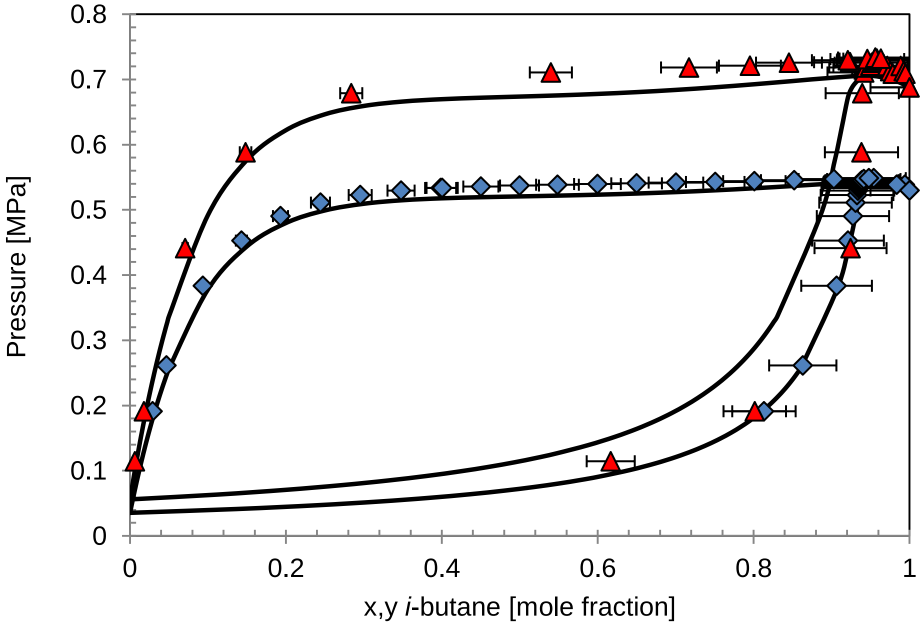

Figure 5.15: Phase equilibria of the binary system i-butane – methanol at 313.06 K (♦) and 323.15 K (▲) **[5.25]**. *(-) GC-PR-CPA model. Error bar: ± 5%*

5.3.3. Naphthenic Hydrocarbons

Naphthenic hydrocarbons – methanol systems form an azeotrope. As seen on Figure 5.16, the model reproduces this behaviour.

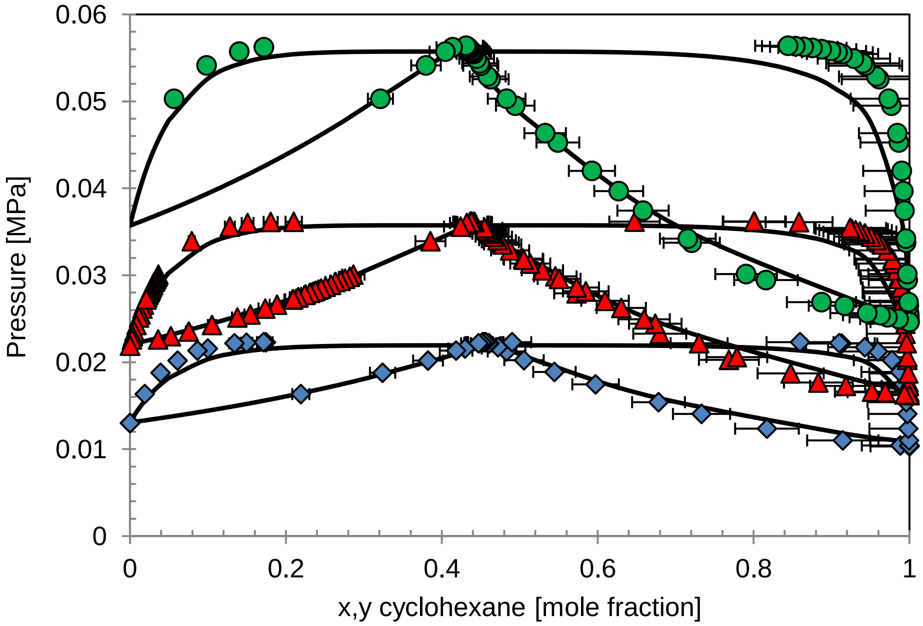

Figure 5.16: Phase equilibria of the binary system cyclohexane – methanol at 293.15 K (♦), 303.15 K (▲) [5.26] and 313.15 K (●) [5.27]. (-) GC-PR-CPA model. Error bar: ± 5%

There are some discrepancies in the vapour phase, but as seen in Table 5.14, the model is globally accurate within the experimental error. However, the model is not able to predict LLE for these systems.

Table 5.14: Deviations between the GC-PR-CPA model and experimental data for naphthenic hydrocarbons – methanol binary systems

Groups	**Compounds**	**AAD [%]**			**Temperature range [K]**	**Pressure range [MPa]**
		P	**y**	**y methanol**		
$CH_{2,cyclic}$	Cyclohexane	4	5	18.5	278 – 333	0.01 – 14
$CH_{2,cyclic}$, CH_{cyclic} / C_{cyclic}	Methylcyclopentane	13	5	11	296 – 345	0.1 – 120
	Methylcyclohexane	2	3	1	298 – 318	0.03 – 0.1

5.3.4. Aromatic Hydrocarbons

The benzene – water system shows an azeotrope. The model is able to reproduce the azeotrope and is in general in good agreement with experimental data, but there are some discrepancies for methanol content. For the other systems, the model is accurate and reproduces the shape of the equilibrium (Figure 5.17), except for *o*-xylene (Table 5.15).

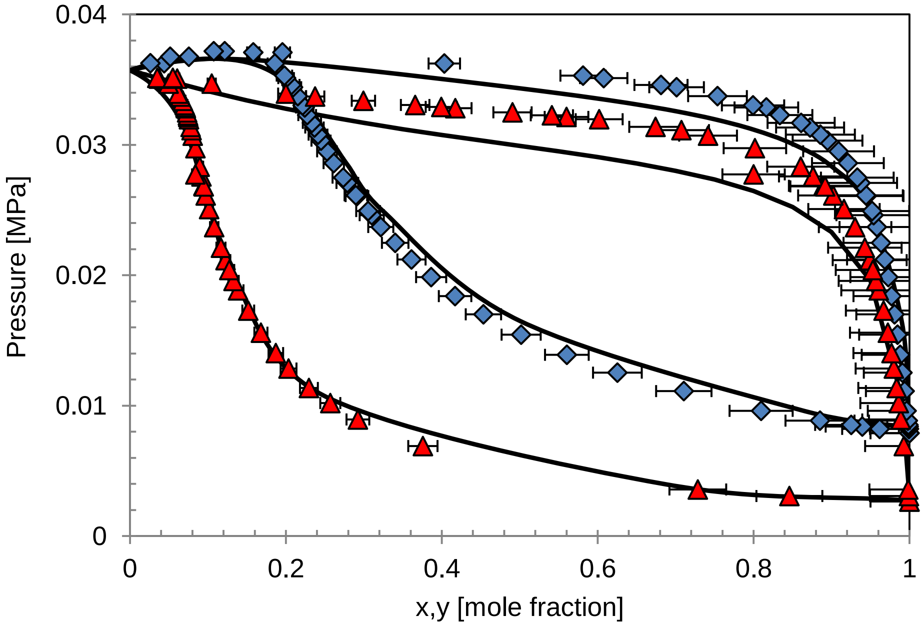

Figure 5.17: Phase equilibria of the binary systems toluene – methanol (♦) and p-xylene – methanol (▲) at 313.15 K **[5.28]**. *(-) GC-PR-CPA model. Error bar: ± 5%*

Table 5.15: Deviations between the GC-PR-CPA model and experimental data for aromatic hydrocarbons – methanol binary systems

Groups	**Compounds**	**AAD [%]**			**Temperature range [K]**	**Pressure range [MPa]**
		P	**y**	**y methanol**		
CH_{aro}	Benzene	5	9	25	298 – 353	0.02 – 0.1
CH_{aro}, C_{aro}	Toluene	4	8	8	313 – 383	0.008 – 0.1
	Ethylbenzene	7	12.5	1	338 – 407	0.1
	o-Xylene	24	49	3	336 – 415	0.1
	p-Xylene	8	11	4	313 – 409	0.003 – 0.01

5.3.5. Gases

As for the methane – methanol system, predictions deviate from experimental data for methanol content in carbon dioxide. The accuracy is greater for the methanol content in hydrogen sulphide and nitrogen, even if discrepancies are observed at higher temperatures. Regarding to gases solubility in methanol, the model is accurate at low pressures, but deviates significantly near the critical region. But this is inherent to the model [5.29]. For the three other systems, their solubility is well reproduced, with some deviations at low temperatures and high pressures, still acceptable with the experimental uncertainty.

Table 5.16: Deviations between the GC-PR-CPA model and experimental data for acid gases – methanol and inert gases – methanol binary systems

Groups	**Compounds**	**AAD [%]**			**Temperature range [K]**	**Pressure range [MPa]**
		P	**y**	**y methanol**		
CO_2	Carbon dioxide	11	3	26	213– 478	0.1 – 19
H_2S	Hydrogen sulphide	6	6	21	223 – 448	2.10^{-4} – 11
N_2	Nitrogen	10	0.4	13.5	213 – 373	0.1 – 108
H_2	Hydrogen	10	0.14	27	213 – 477	0.04 – 110

5.3.6. Alcohols

As seen in Table 5.17, the model is in relative good agreement for alcohol – methanol systems. Their behaviour is accurately reproduced within the experimental error.

Table 5.17: Deviations between the GC-PR-CPA model and experimental data for alcohols – methanol binary systems

Groups	**Compounds**	**AAD [%]**			**Temperature range [K]**	**Pressure range [MPa]**
		P	**y**	**y alcohol**		
$CH_{3,OH}$, $CH_{2,OH}$, OH	*n*–Propanol	4	4	7	273 – 370	5.10^{-4} – 0.1
	n–Butanol	6	5	22	298 – 559	0.001 – 7
	n–Pentanol	8	4	24	313 – 410	9.10^{-4} – 0.1
	n-Decanol	10	-	-	293 – 323	$2..10^{-6}$ – 0.06

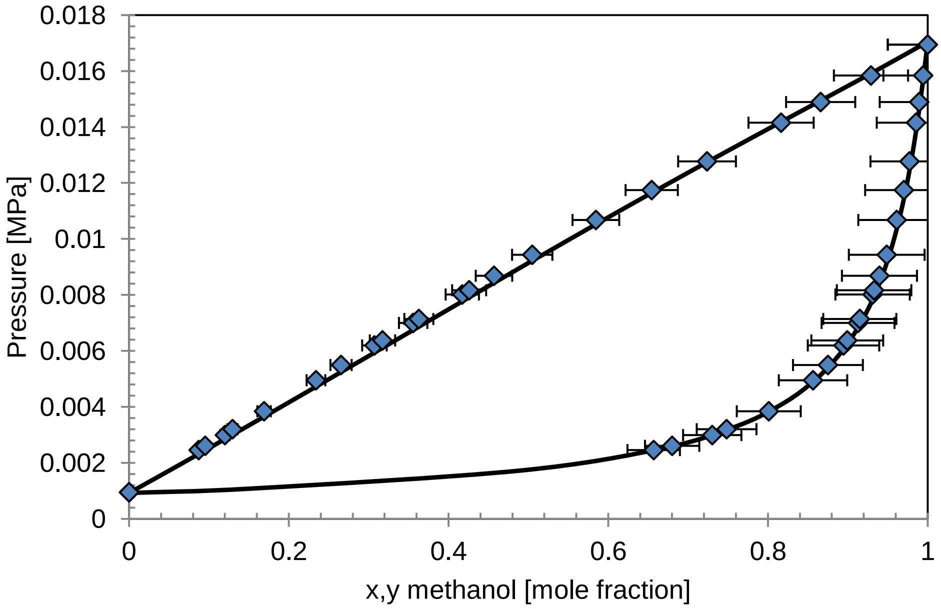

Figure 5.18: Phase equilibria of the binary systems n-butanol – methanol at 298.15 K (♦) **[5.30]**. *(-) GC-PR-CPA model. Error bar: ± 5%*

5.4. BINARY SYSTEMS WITH ETHANOL

Ethanol is also a hydrate inhibitor and therefore its behaviour with hydrocarbons and gases is of interest.

5.4.1. Normal Alkanes

Flash and bubble point calculations have been used to determine group parameters for *n*-alkane – ethanol systems. As seen in Table 5.18, the model seems to deviate a lot for methane – ethanol and ethane – ethanol systems. In fact, it fails near and in the critical region, which is inherent to the model. The same analysis can be done for the propane – ethanol system.

Referring to Table 5.19, the model is in general in good agreement with experimental data for other alkanes and reproduces the azeotropic behaviour of *n*-alkane – ethanol systems (with $5 \leq n \leq 8$).

Table 5.18: Deviations between the GC-PR-CPA model and experimental data for methane – ethanol and ethane – ethanol binary systems

Groups	**Compounds**	**AAD [%]**			**Temperature range [K]**	**Pressure range [MPa]**
		x	**y**	**y ethanol**		
CH_4	Methane	10	5	12	280 – 498	0.5 – 36
C_2H_6	Ethane	21	5	18	298 – 498	0.3 – 12

Table 5.19: Deviations between the GC-PR-CPA model and experimental data for normal alkanes – ethanol binary systems

Groups	**Compounds**	**AAD [%]**			**Temperature range [K]**	**Pressure range [MPa]**
		P	**y**	**y ethanol**		
CH_3, CH_2	Propane	10.5	1.5	20.5	273 – 500	0.03 – 6
	n-Butane	11	0.7	9	283 – 500	0.006 – 9
	n-Pentane	12	8	6	303 – 500	0.03 – 6
	n-Hexane	7	4	4.5	298 – 508	0.01 – 6

Table 5.19 (to be continued): Deviations between the GC-PR-CPA model and experimental data for normal alkanes – ethanol binary systems

Groups	**Compounds**	**AAD [%]**			**Temperature range [K]**	**Pressure range [MPa]**
		P	**y**	**y ethanol**		
CH_3, CH_2	*n*-Heptane	6	8	6	303 – 523	0.004 – 6
	n-Octane	9	6	2	308 – 359	0.004 – 0.1
	n-Nonane	5	3.5	0.4	343	0.006 – 0.07
	n-Decane	3	11	2	307 – 447	0.1
	n-Undecane	12	35	0.8	333 – 353	6.10^{-4} – 0.1

5.4.2. Branched Alkanes

Limited data are available for branched alkanes with ethanol systems. However, as seen in Table 5.20, the model is in good agreement with the experimental data found, for the limited range of temperature and pressure.

Table 5.20: Deviations between the GC-PR-CPA model and experimental data for branched alkanes – ethanol binary systems

Groups	**Compounds**	**AAD [%]**			**Temperature range [K]**	**Pressure range [MPa]**
		P	**y**	**y ethanol**		
CH_3, CH_2, CH	*i*-Butane	1	0.3	4	309 – 364	0.02 – 2
	i-Pentane	3	7	3	300 – 352	0.02 – 0.2
	2,3-Dimethylbutane	2.5	2	2.5	325 – 343	0.1

5.4.3. Naphthenic Hydrocarbons

Figure 5.19 illustrates the accuracy of the model for naphthenic hydrocarbons with ethanol systems. The model reproduces the azeotropic behaviour and is in good agreement with experimental data within the experimental error (Table 5.21) in the limited range of pressure and temperature of data found.

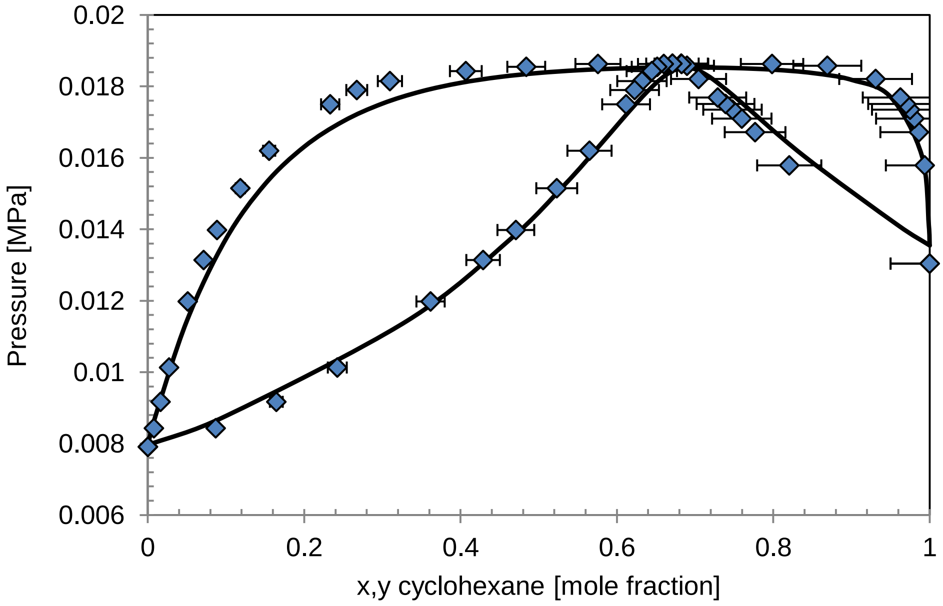

Figure 5.19: Phase equilibria of the binary systems cyclohexane – ethanol at 298.15 K (♦) [5.31]*. (-) GC-PR-CPA model. Error bar: ± 5%*

Table 5.21: Deviations between the GC-PR-CPA model and experimental data for naphthenic hydrocarbons – ethanol binary systems

Groups	**Compounds**	**AAD [%]**			**Temperature range [K]**	**Pressure range [MPa]**
		P	**y**	**y ethanol**		
$CH_{2,cyclic}$	Cyclopentane	3	1.5	5	323 – 374	0.1 – 0.5
	Cyclohexane	2	3.5	6	278 – 338	0.002 – 0.1
$CH_{2,cyclic}$, CH_{cyclic} / C_{cyclic}	Methyl-cyclopentane	1	3	3	333 – 349	0.1
	Methyl-cyclohexane	1	3	2	345 – 369	0.1

5.4.4. Aromatic Hydrocarbons

As for systems with water and methanol, the model is in good agreement with experimental data for benzene – ethanol, toluene – ethanol and ethylbenzene – ethanol systems. However, deviations are more important for xylene – ethanol systems.

Table 5.22: Deviations between the GC-PR-CPA model and experimental data for aromatic hydrocarbons – ethanol binary systems

Groups	**Compounds**	**AAD [%]**			**Temperature range [K]**	**Pressure range [MPa]**
		P	**y**	**y ethanol**		
CH_{aro}	Benzene	2.5	4	5	294 – 347	0.008 – 0.1
CH_{aro}, C_{aro}	Toluene	7	13	5	286 – 383	0.004 – 0.1
	Ethylbenzene	3	10	2	350 – 409	0.1
	m-Xylene	34	76	50	298 – 408	0.004 – 0.1
	o-Xylene	12	29	22	308 – 411	0.003 – 0.1
	p-Xylene	13	22	7	313 – 409	0.003 – 0.1

An example is shown on Figure 5.20.

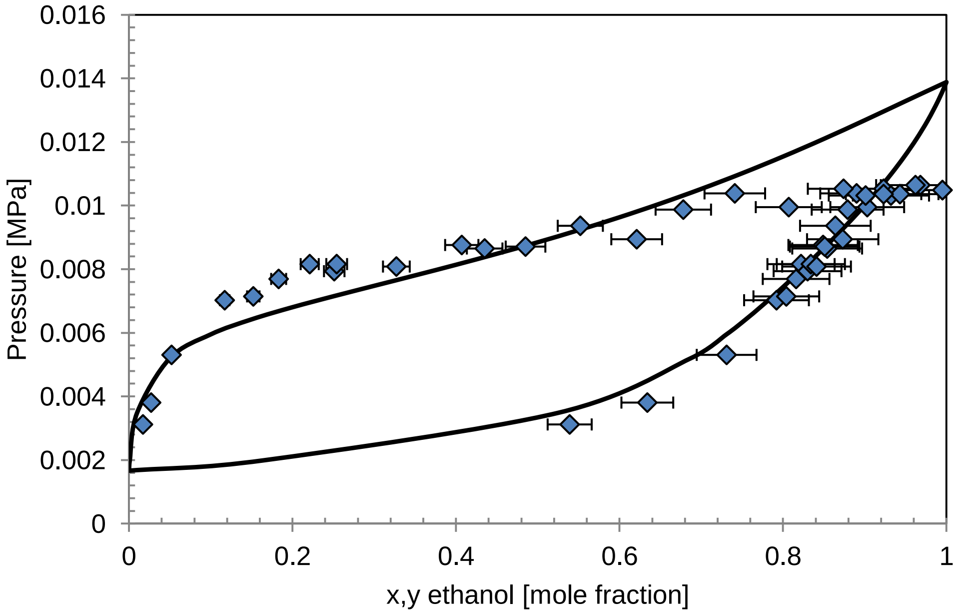

Figure 5.20: Phase equilibria of the binary systems o-xylene – ethanol at 308.15 K (♦) **[5.32]**. *(-) GC-PR-CPA model. Error bar: ± 5%*

Limited data are available, and in the case of *o*-xylene – ethanol system the shape seems to be incoherent. Indeed, the vapour pressure of ethanol at 308.15 K is 0.0138 MPa, according to Scatchard and Satkiewicz **[5.33]** and Singh and Benson **[5.34]**. But data show a vapour pressure at 0.01 MPa, explaining the difference in the shape of the equilibrium.

5.4.5. Gases

For acid gases, only data for carbon dioxide have been found. The model is accurate only in the subcritical region and over predicts the critical region. For the nitrogen – ethanol system, the model over predicts ethanol content, but is accurate for nitrogen solubility. As for hydrogen, the model is accurate in general, but there are discrepancies at high temperatures and high pressures.

Table 5.23: Deviations between the GC-PR-CPA model and experimental data for carbon dioxide – ethanol and inert gases – ethanol binary systems

Groups	**Compounds**	**AAD [%]**			**Temperature range [K]**	**Pressure range [MPa]**
		x	**y**	**y ethanol**		
CO_2	Carbon dioxide	18	2	48	283 – 496	0.09 – 15
N_2	Nitrogen	6	0.9	38	298 – 398	0.1 – 10
H_2	Hydrogen	15	13	10	213 – 508	0.1 – 34

5.5. BINARY SYSTEMS WITH ALCOHOLS

Alcohols have also been added to the model but parameters adjustment is still in progress. It has been done for water – alcohol (see *5.2.8*), alcohol – alcohol and methane- alcohols binary systems

5.5.1. Normal Alkanes

Limited data are available for methane – alcohol systems. Deviations are presented in Table 5.24. The model in in good agreement with experimental data but presents some deviations in alcohol content representation.

Table 5.24: Deviations between the GC-PR-CPA model and experimental data for alkanes – alcohols binary systems

Alkane	**Alcohols**	**AAD [%]**			**Temperature range [K]**	**Pressure range [MPa]**
		x	**y**	**y alcohol**		
Methane	*n*-Propanol	2	0.1	26	313 – 333	1 – 10
	n-Heptanol	6	-	-	298	0.1

5.5.2. Alcohols

Table 5.25 presents deviations for alcohol – alcohol systems. The model is accurate for all these systems. There are some discrepancies at higher temperatures, but behaviours are well represented in general.

Table 5.25: Deviations between the GC-PR-CPA model and experimental data for alcohol – alcohol binary systems

Alcohol (1)	**Alcohol (2)**	**AAD [%]**			**Temperature range [K]**	**Pressure range [MPa]**
		P	**y_1**	**y_2**		
n -Propanol	*n*-Butanol	1	1.5	1	313 – 391	3.10^{-3} – 0.1
	n-Pentanol	2	2	10	313 – 411	9.10^{-4} – 0.1
	n-Hexanol	1	-	-	356 – 411	0.05 – 0.1
	n-Decanol	5	-	-	293 – 323	2.10^{-6} – 0.01
n -Butanol	*n*-Pentanol	5	5	17	313 – 371	9.10^{-4} – 0.02
n -Hexanol	*n*-Pentanol	7	2	5	331 – 388	3.10^{-3} – 0.02
	n-Heptanol	10	3	5	344 – 406	3.10^{-3} – 0.02
	n-Octanol	2	1	8	356 – 391	4.10^{-3} – 0.01
n-Octanol	*n*-Nonanol	8	2	3	361 – 418	1.10-3 – 0.01

5.6. VAPOUR-LIQUID EQUILIBRIUM OF MULTICOMPONENT SYSTEMS

The model is tested here for multi-component systems. First, two ternary systems are considered, including the three principal associating compounds studied in this work, water, methanol and ethanol. Then predictions for a more complex system with water are presented.

5.6.1. Ternary Systems

The first ternary system is a mixture of methane, water and methanol. The feed composition is presented in Table 5.26. This system has been studied over three temperatures (280.25, 298.77 and 313.45 K).

Table 5.26: Feed composition of each component (mole %) of MIX 8 **[5.35]**

Compounds	**MIX 8**
Methane	25.0
Water	46.3
Methanol	28.7

Table 5.27: Deviations between the GC-PR-CPA model and experimental data for MIX 8

Compounds	**Absolute Error [mole fraction]**		**AAD [%]**	
	x*10^{-3}	**y*10^{-4}**	**x**	**y**
Methane	3.6	3.9	47	0.04
Water	0.29	0.66	0.05	9.2
Methanol	4	3.9	1.1	9.1

Deviations between experimental and predicted data are given in Table 5.27. The model presents important deviations for methane composition in the liquid phase. But as seen in *5.3*, there are more discrepancies in the predictions of hydrocarbons solubilities in methanol at low temperatures, conditions met here. It would explain this high deviation.

Another mixture composed of water, methanol and ethanol **[5.36]** is studied. Experimental measurements have been done at atmospheric pressure at several temperatures. Pressure and vapour compositions have been predicted and deviations are given in Table 5.28.

Table 5.28: Deviations between the GC-PR-CPA model and experimental data for MIX 9

Compounds	**Absolute Error [mole fraction]**		**AAD [%]**	
	P	**y*10^{-2}**	**P**	**y**
Water	$3.05.10^{-3}$	1.2	3.0	6.4
Methanol		1.2		4.1
Ethanol		1.8		5.8

As seen in Table 5.28, the model is in good agreement with experimental data for methanol in vapour phase, considering an experimental error of 5% and for bubble pressure. Deviations for water and ethanol in the vapour phase are mainly due to the discrepancies already seen for the water –ethanol binary system, but predictions are still acceptable, since it is close to 5%.

5.6.2. Multicomponent System

Water distribution in gas production systems has been studied few years ago **[5.37]**. One of the multicomponent systems, defined in Table 5.29 as MIX 10, is considered here to validate the model. The system MIX 10 + water shows vapour – liquid – liquid equilibrium at pressures and temperatures of study.

Table 5.29: Composition of each component (mole %) of mixture MIX 10 [5.37]

Compounds	MIX 10
Methane	23.5
Ethane	5.6
Propane	8.9
***n*-Butane**	8.9
***n*-Heptane**	13.1
***n*-Decane**	16.4
Toluene	23.6

Deviations between experimental and predicted data are given for both organic and vapour phases.

Table 5.30: Deviations between the GC-PR-CPA model and experimental data for MIX 10

Compounds	Absolute Error [mole fraction]		AAD [%]		EE[%]	
	$x*10^{-3}$	**$y*10^{-3}$**	**x**	**y**	**x**	**y**
Methane	11.4	20.3	16.2	2.7	12	3
Ethane	1.2	7.3	4.7	7.0	12	5
Propane	7.8	18.5	9.0	9.3	14	5
***n*-Butane**	1.3	3.7	1.2	15.5	11	10

Table 5.30 (to be continued): Deviations between the GC-PR-CPA model and experimental data for MIX 10

Compounds	**Absolute Error [mole fraction]**		**AAD [%]**		**EE[%]**	
	$x*10^{-3}$	**$y*10^{-3}$**	**x**	**y**	**x**	**y**
***n*-Heptane**	4.1	0.39	2.3	24.3	11	15
***n*-Decane**	4.0	0.013	1.9	15.2	10	15
Toluene	5.2	0.47	1.7	23.7	8	15
Water	1.1	0.25	139	10.6	12	15

Considering the organic phase, the model is in general in good agreement with experimental data, within experimental errors (Figure 5.22). However, the model over predicts methane composition (Figure 5.21), and fails significantly to predict water composition (over prediction with an order of magnitude of 10).

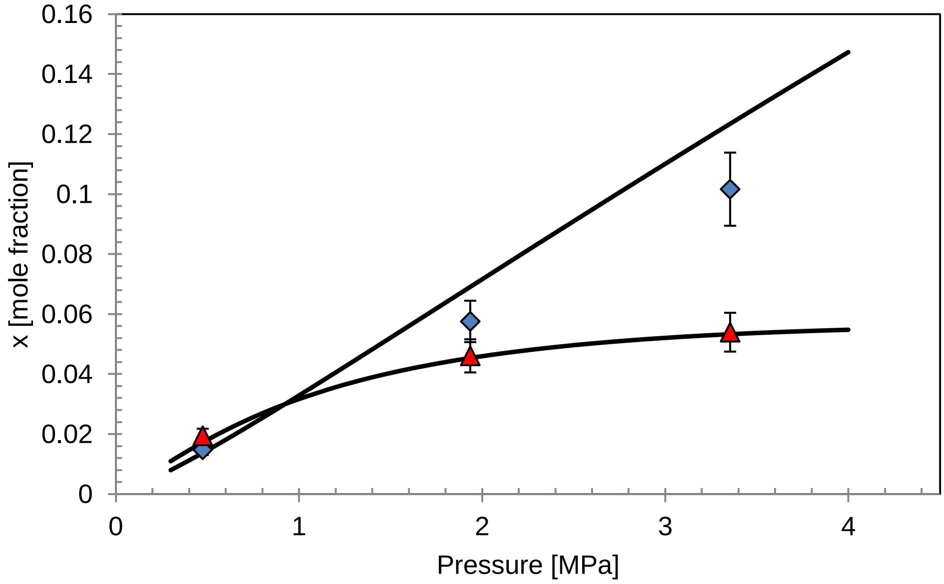

Figure 5.21: Compositions of methane (♦) and ethane (▲) in organic phase of MIX 10 at 298.1 K. (-) GC-PR-CPA model. Error bar from [5.37]: ± 12%

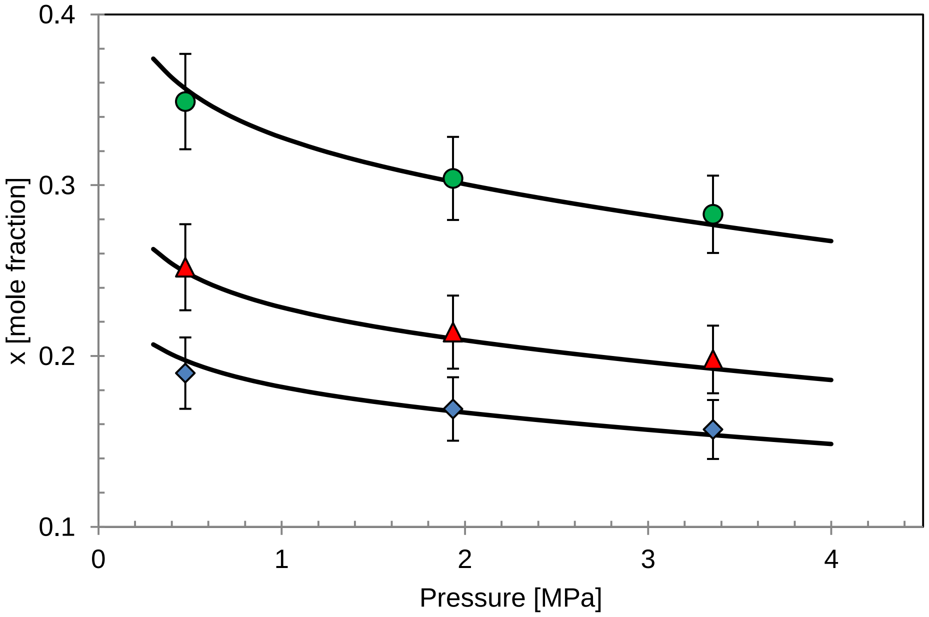

Figure 5.22: Compositions of n-heptane (♦), n-decane (▲) and toluene (●) in organic phase of MIX 10 at 298.1 K. (-) GC-PR-CPA model. Error bars from [5.37]: ± 11%, ± 10% and ± 8%.

As for the vapour phase, the model is in general in good agreement with experimental data, within the experimental error (see Figure 5.23 and Figure 5.24).

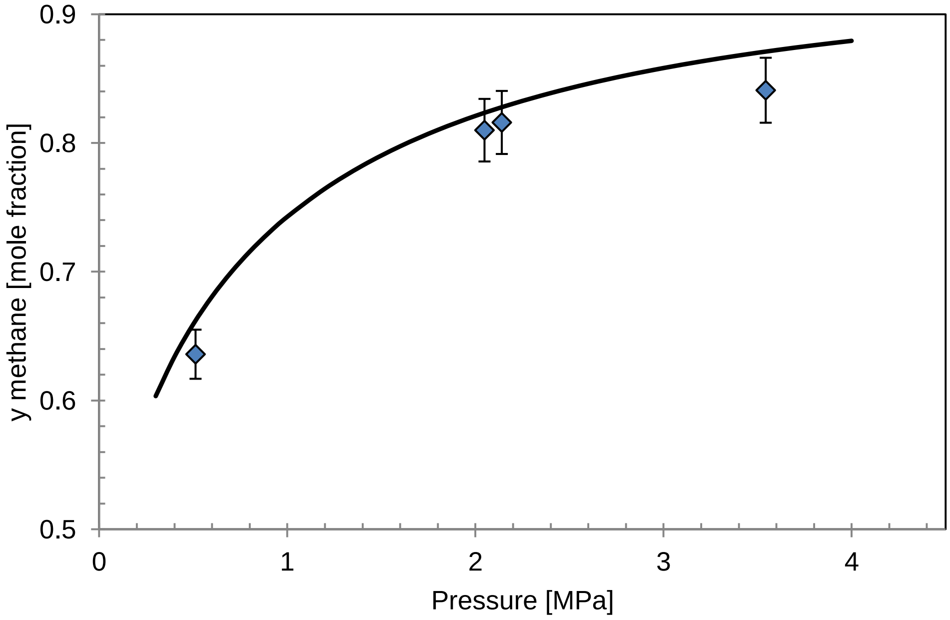

Figure 5.23: Compositions of methane (♦) in vapour phase of MIX 10 at 298.1 K. (-) GC-PR-CPA model. Error bar from [5.37]: ± 3%

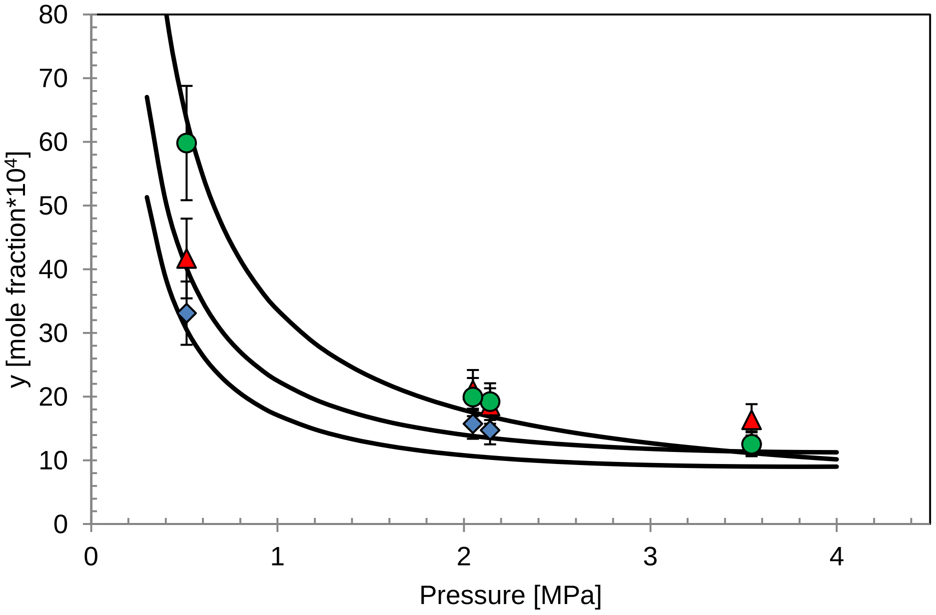

Figure 5.24: Compositions of n-heptane (♦), toluene (▲) and water (●) in vapour phase of MIX 10 at 298.1 K. (-) GC-PR-CPA model. Error bar from [5.37]: ± 15%

5.7. HYDRATE STABILITY ZONE

Hydrate dissociation points have been measured for eight systems. Predictions of hydrate dissociation curves are presented here for two systems with and without hydrate inhibitors.

5.7.1. Binary System

Hydrate stability zone for the binary system 80% methane + 20% hydrogen sulphide is predicted here with the GC-PR-CPA model. As seen on Figure 5.25, predictions must be calculated for the different aqueous fractions defined to better represent experimental data.

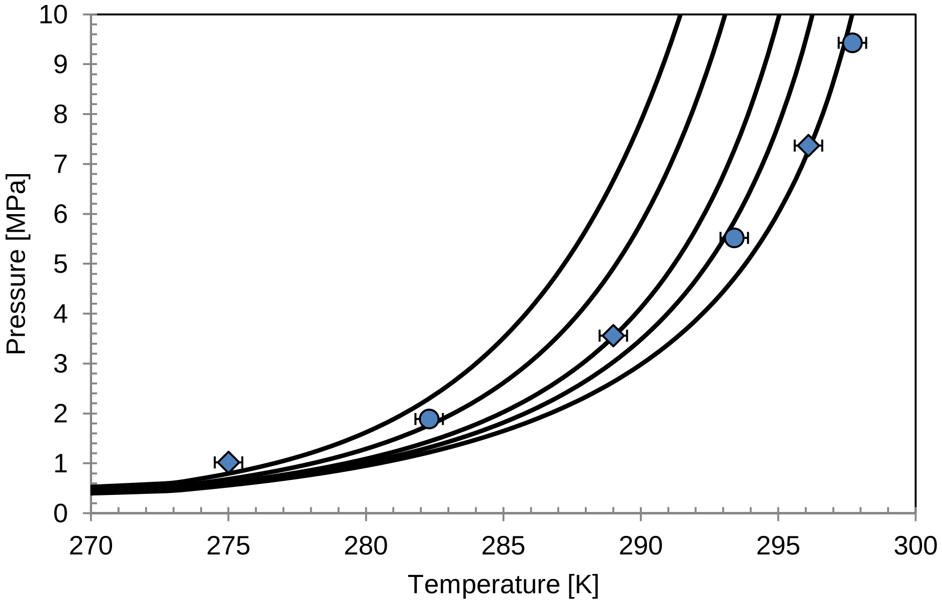

Figure 5.25: Hydrate dissociation points of 80% methane + 20% hydrogen sulphide system. (-) GC-PR-CPA model for different aqueous fractions (from the left to the right: 0.98, 0.96, 0.94, 0.91, 0.82). Error bar: ± 0.5 K.

5.7.2. Multicomponent System

Hydrate stability zone is also predicted for MIX 5 with deionised water. As seen on Figure 5.26, the model is in good agreement with experimental data.

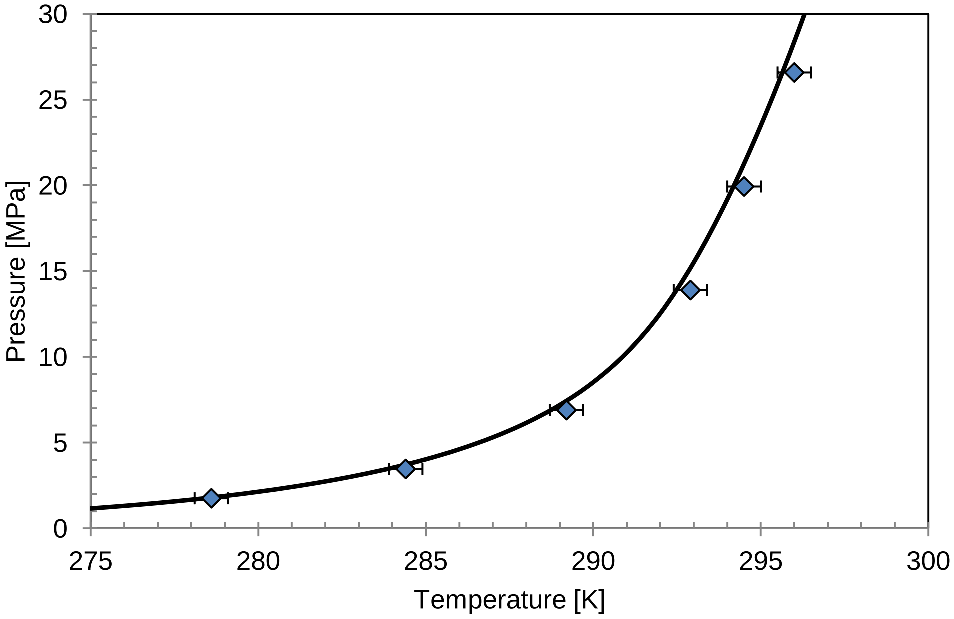

Figure 5.26: Hydrate dissociation points of MIX 5 with deionised water. (-) GC-PR-CPA model. Error bar: ±0.5 K.

When considering thermodynamic inhibitors, the model is in good agreement with experimental data for MIX 5 with 25%$_{wt}$ of methanol but presents some discrepancies for the mixture with 25%$_{wt}$ of ethanol (see Figure 5.27). It is certainly related to the deviations already seen in phase equilibria predictions. It is also relatively accurate for higher concentrations of methanol, with small deviations at low temperatures (Figure 5.28), but presents higher deviations for systems with ethanol.

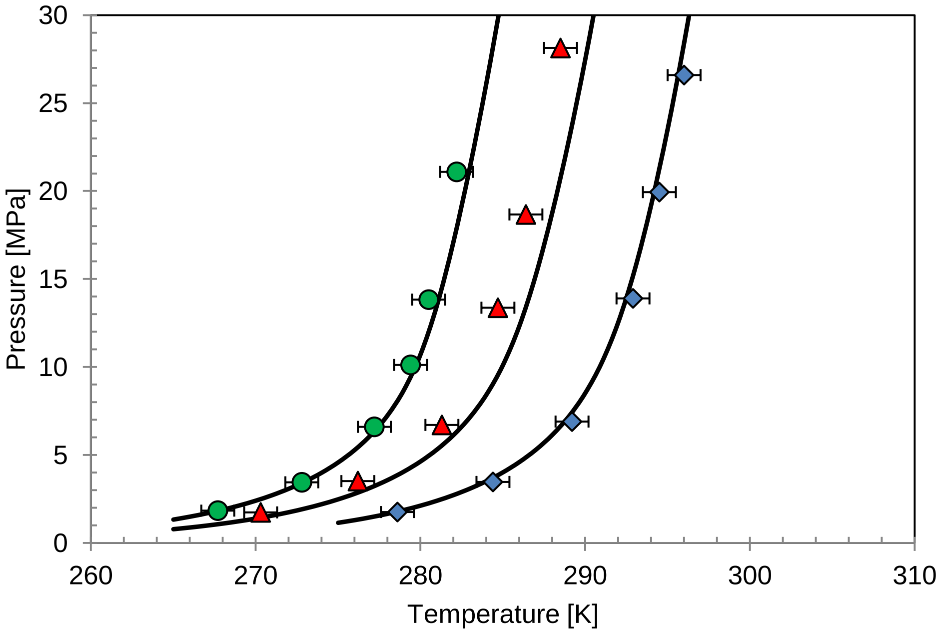

Figure 5.27: Hydrate dissociation points of MIX 5 with deionised water (♦), 25%$_{wt}$ ethanol (▲) and 25%$_{wt}$ methanol (●). (-) GC-PR-CPA model. Error bar: ±0.5 K.

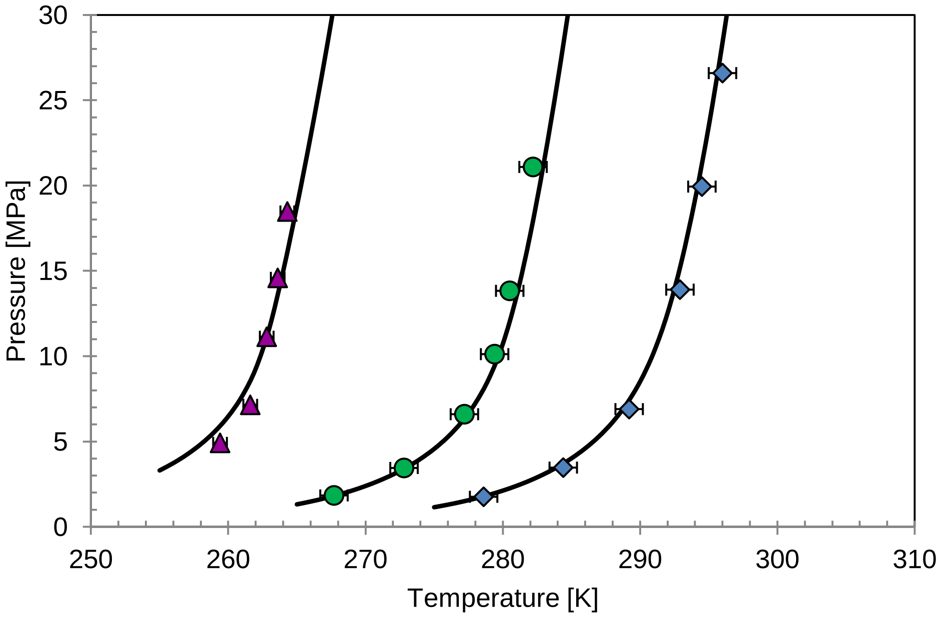

Figure 5.28: Hydrate dissociation points of MIX 5 with deionised water (♦), 25%$_{wt}$ methanol (●) and 50%$_{wt}$ methanol (▲). (-) GC-PR-CPA model. Error bar: ±0.5 K.

5.8. ENTHALPIES OF MIXING

5.8.1. Definition

The enthalpy of mixing represents the non ideality of the mixture. For mixtures with few polar and few associating compounds (e.g. alkane mixtures), h^M is negligible. But it is not the case for systems with water (e.g. hydrocarbons – water mixtures), which are asymmetrical systems and present highly nonideal behaviour.

The enthalpy of mixing, and not the excess enthalpy as it is mistakenly named by some authors **[5.38]**, can be experimentally measured with a calorimeter.

The enthalpy of mixing of N components systems at a given temperature T, pressure P and composition z is given by Equation (5.4) **[5.38]**.

$$h^M(T,P,z) = h(T,P,z) - \sum_{i=1}^{N} z_i h_{i,pure}^{stable\ state}(T,P) \tag{5.4}$$

Where $h_{pure,i}^{stable\ state}(T,P)$ is the molar enthalpy of a pure compound i at the same conditions (T and P) as the mixture in its stable state. .

As for the excess enthalpy, it can be expressed in function of the mixing enthalpy:

$$h^E(T,P,z) = h^M(T,P,z) - h^{M,id}(T,P,z) \tag{5.5}$$

where $h^{M,id}$ is:

$$h^{M,id}(T,P,z) = \sum_{i=1}^{N} z_i \left[h_{i,pure}^{same\ state\ as\ the\ mixture}(T,P) - h_{i,pure}^{stable\ state}(T,P)\right] \tag{5.6}$$

When the mixture is ideal and the pure compounds are in the same state as the mixture, $h^{M,id}$ is equal to zero. It is the restricted case where the enthalpy of mixing is equal to the excess enthalpy.

5.8.2. Predictions of Enthalpies of Mixing

Enthalpies of mixing are predicted for three binary systems with water at different temperatures and pressures. The compounds chosen refer to the different families presented previously: hydrocarbons with propane and benzene and gases with nitrogen.

The first system is water – propane at atmospheric pressure. As seen on Figure 5.29, the model is in good agreement with experimental data, within the experimental error.

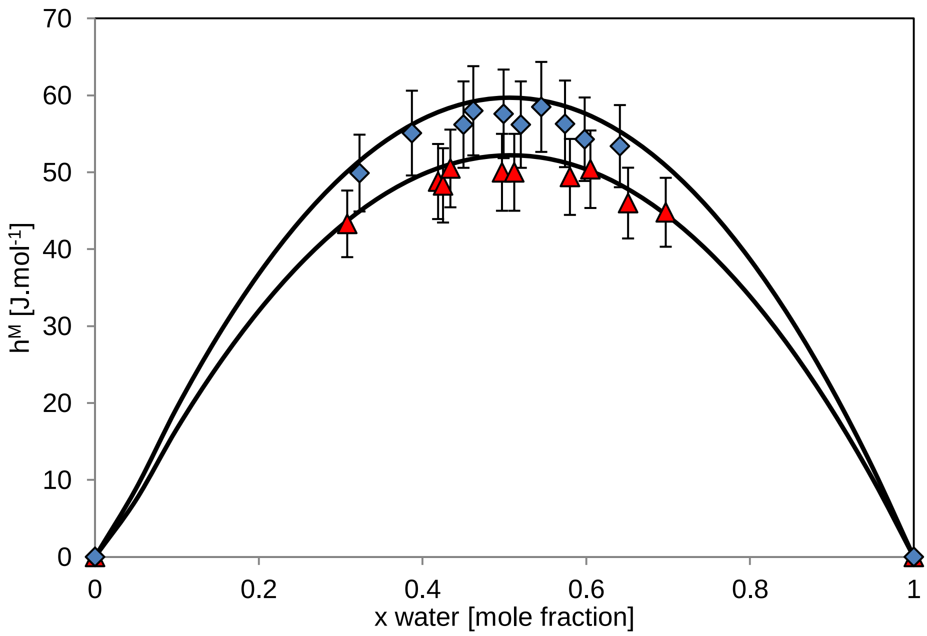

Figure 5.29: Enthalpies of mixing at atmospheric pressure of the binary system water – propane at 383.2 K (♦) and 393.2 K (▲) **[5.39]**. *(-) GC-PR-CPA model. Error bar: ± 10%.*

The AAD is 3% for enthalpies of mixing at 383.2 K and 4% at 393.2 K and the AAE is respectively 1.3 J.mol^{-1} and 2.1 J.mol^{-1}, which is accurate.

Figure 5.30 presents enthalpies of mixing of the system water – benzene at two temperatures. The maximum experimental value at 581 K is 11.2 kJ.mol^{-1} and 13.5 kJ.mol^{-1} at 592 K. The model over predicts the enthalpies of mixing at 581 K and gives a maximum of 11.9 kJ.mol^{-1}, while it under predicts at 592 K, giving a maximum of 12.4 kJ.mol^{-1}.

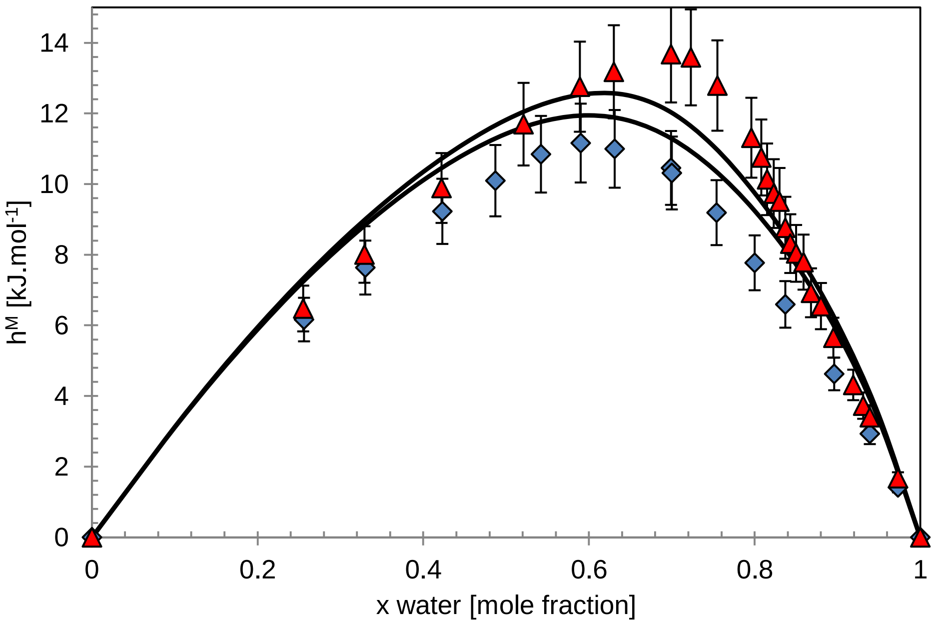

Figure 5.30: Enthalpies of mixing at 16.4 MPa of the binary system water – benzene at 581 K (♦) and 592 K (▲) **[5.40]**. *(-) GC-PR-CPA model. Error bar: ± 10%.*

There are more discrepancies for this system, with 14% deviation for values at 581 K and 9% at 592 K, the AAE are respectively 1.1 kJ.mol^{-1} and 0.8 kJ.mol^{-1}. Maximum deviation usually accepted is 10%, so some improvements should be done to reduce deviations.

Figure 5.31 shows predicted and experimental enthalpies of mixing for the water – nitrogen system.

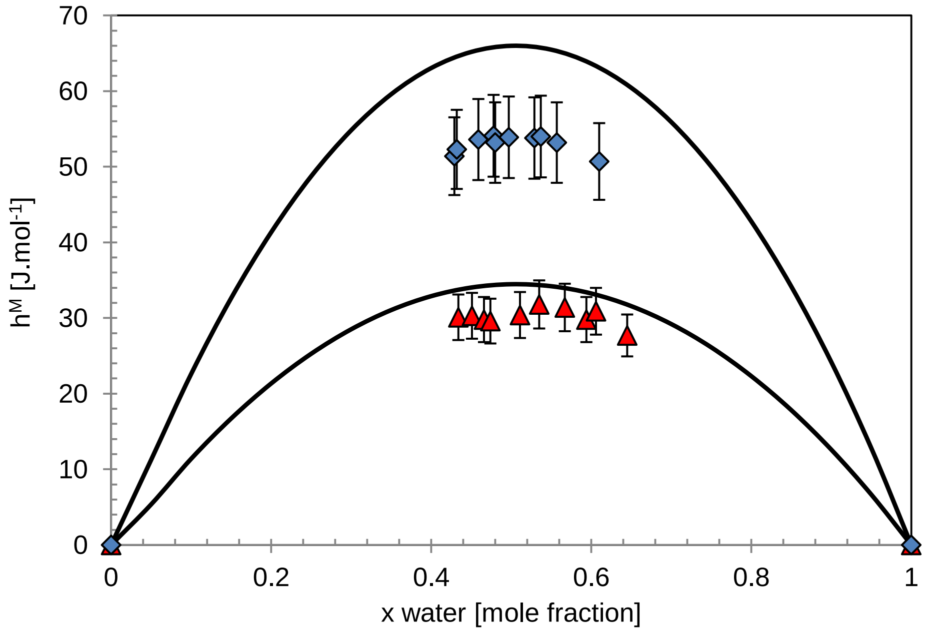

Figure 5.31: Enthalpies of mixing at atmospheric pressure of the binary system water – nitrogen at 373.15 K (♦) and 423.15 K (▲) **[5.41]**. *(-) GC-PR-CPA model. Error bar: ± 10%.*

The model is in good agreement with experimental data at 423.15 K, with 10.6% and an AAE of 3.6 J.mol^{-1}. However, there are 18.7% deviations at 373.15 K and the AAE is equal to 12.2 J.mol^{-1}. These deviations can be related to the ones observed for nitrogen solubility in water: there are 9% deviations at 373.15 K against 0.6% at 423.15 K.

The GC-PR-CPA model has not taken into account enthalpies of mixing in parameters adjustments. For the three systems presented and in general, the model presents satisfactory results. But it can be improved to reduce deviations seen in some systems and to have good predictions whatever the mixture considered.

For liquid mixture, Desnoyers and Perron **[5.42]** suggested to plot the $h^E/(x_1x_2)$ instead the excess enthalpy itself. As the excess enthalpy represents the nonideality of mixtures, plotting the total apparent molar thermodynamic quantity $h^E/(x_1x_2)$ helps to identify the difference in interactions. Excess enthalpies at 323.15 K are presented on Figure 5.32 for the water – ethanol binary system. $h^E/(x_1x_2)$ versus water mole fraction is plotted on

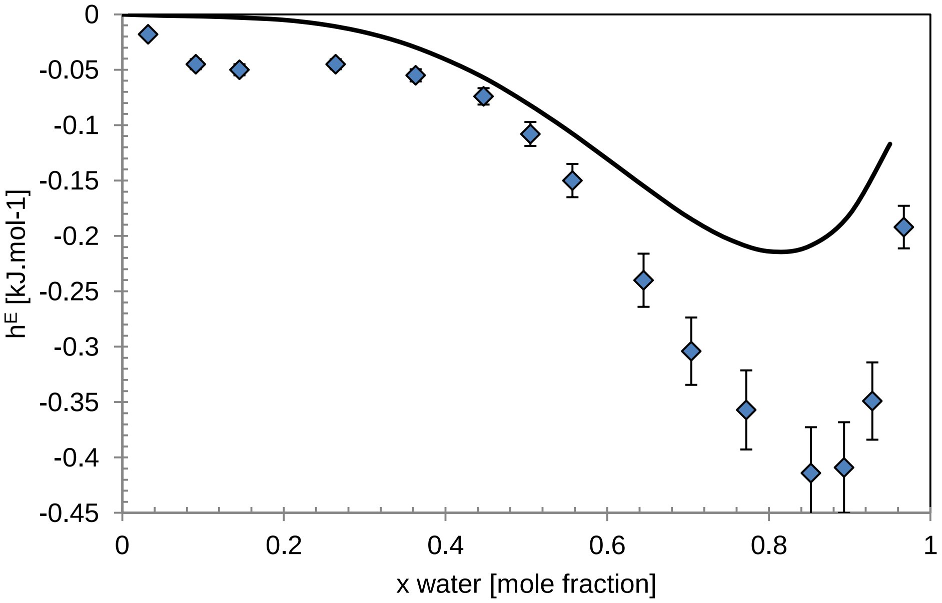

Figure 5.32: Excess enthalpies at atmospheric pressure of the water – ethanol binary system at 323.15 K **[5.43]**. *(-) GC-PR-CPA model. Error bar: ± 10%.*

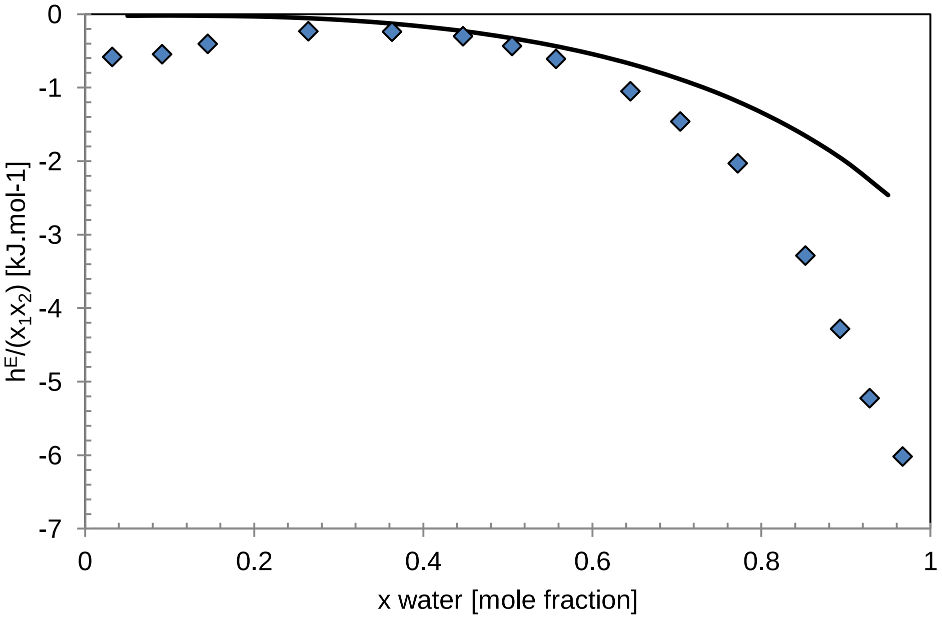

Figure 5.33: Total apparent molar thermodynamic quantity of the water – ethanol binary system at 323.15 K **[5.43]**. *(-) GC-PR-CPA model.*

The model is able to reproduce the particular shape of the excess enthalpy for the water – ethanol system. However it presents important discrepancies with 54% of deviations, the AAE being 89.2 J.mol^{-1}. These discrepancies are principally present at higher water molar fraction as for phase equilibria. From Figure 5.33 and the different trends presented by Desnoyers and Perron **[5.42]**, we can deduce that this system belongs to mixtures of liquids of different size and polarity, which is the case from a molecular point of view.

5.9. CONCLUSION

In this chapter, the accuracy of the model has been evaluated for several binary systems containing water and alcohols, over a wide range of temperature and pressure conditions. The model has been validated using independent experimental data. The GC-PR-CPA model is able to predict mutual solubilities of hydrocarbons, acid gases and inert gases with water and alcohols. Phase diagrams of water – alcohol and alcohol – alcohol have also been considered. In general, the model is in good agreement with experimental data, within the experimental error and is better for VLE than for LLE.

In this chapter, the ability of the model to predict VLE and hydrate stability zone for multicomponent systems have been evaluated. For systems with water, the model is in good agreement with experimental data. For mixtures with methanol or ethanol, the discrepancies seen in binary mixtures are also present in multi-component systems. Mixing enthalpies have also been considered for binary systems. Since enthalpies have not been taken into account in parameters adjustments, the model can be considered in good agreement with experimental data. However, it can be improved by adding enthalpies in the objective function. But it may degrade VLE and LLE predictions.

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CONCLUSION AND PERSPECTIVES

The interest for new gas fields with high content of acid gases and carbon dioxide capture and storage are one of today challenges. It leads to two main considerations: better understanding and prediction of the phase behaviour of mixtures present for an optimized and safe design, and prevention the different issues that may happen. The problem considered in this thesis is hydrates formation during transport due to the presence of water in suitable temperature and pressure conditions.

This thesis includes three aspects related to three industrial projects. The first one is mainly focused on gas hydrate formation in subsea pipelines in the presence of different concentrations of sour and acid gases. This project includes different studies like the impact of thermodynamic inhibitors on hydrate stability zone, inhibitor distribution in water and hydrate formation in low water content. The development of the thermodynamic model is part of this project. The second project is focused on the impact of impurities on carbon dioxide recovered from power plants. Their presence during transport may lead to flow assurance issues, such as gas hydrate formation. The aim of this project is to study the phase behaviour of carbon dioxide in the presence of impurities, to determine the hydrate stability zone and to measure and predict different physical properties such as viscosity and density. Finally the aim of the third project is to investigate the impact of aromatics on acid gas injection. When the natural gas is produced, acid gases are usually removed with different types of amines before being compressed for injection in underground formations. However, amines can also absorb aromatic compounds, which can condense at high pressures and lead to liquid formation in compressors or hydrate formation. This project includes experimental measurements, principally VLE and VLLE with water, but also hydrates dissociation points.

Counting of the experience in thermodynamic modelling of the Centre for Gas Hydrate Research and the Centre Thermodynamic of Processes, a predictive model, called GC-PR-CPA, has been developed. The Cubic-Plus-Association equation of state takes into account hydrogen bonding between associating molecules (e.g. water, alcohols, glycols). The combination with the PPR78 model aims to give predictive feature to the model. After a modification of the expression of binary interaction parameter for associating compounds, group parameters have been adjusted on solubility or bubble point data for binary systems containing water, methanol or ethanol and to a lesser extent other alcohols. Solvation phenomenon has been taken into account for carbon dioxide – water and hydrogen sulphide – water systems. It has been shown that it improves predictions, especially at higher pressures. Indeed, the solubility of gases is more important at higher pressures involving a stronger effect of solvation phenomenon.

The model has been validated using experimental data, taken from the literature, in a wide range of temperatures and pressures. It has been shown that it is able to predict mutual solubilities of hydrocarbons, acid gases and inert gases with water and alcohols, being better for VLE than for LLE. The model fails to predict phase equilibria near the critical region, but this is inherent to cubic equations of state and to the model. Temperature range of hydrate phase boundaries is usually lower than the one of VLE or LLE. Therefore, freezing points have been used as well as phase equilibria data to readjust group interaction parameters for methanol – water and ethanol – water systems, allowing freezing points predictions (with an accuracy between 1 and 1.5%) and better predictions of hydrate stability zone.

To evaluate the model for more complex systems, experimental measurements have been conducted. New experimental measurements of the locus of incipient hydrate curve for systems containing natural gases or acid gases with distilled water or aqueous solution of inhibitors (i.e. methanol, ethanol and ethylene glycol) in a wide range of concentrations, pressures and temperatures have been determined. VLE data and bubble points have also been measured.

Finally, the model has been tested on VLE for multicomponent systems. The model is in general in good agreement with experimental data. Deviations observed are related to the one already noted for binary systems. The ability of the model to predict hydrate stability zone has also been considered. For systems involving water and methanol, the model is in good agreement with experimental data. Higher deviations are observed for systems ethanol: compared to systems with water or methanol, predictions for binary mixtures with ethanol present higher deviations. Finally, the ability of the model to predict enthalpies of mixing has been considered. The model is more or less in good agreement with experimental data, depending on systems, temperature and pressure conditions considered. But these results are, in general, satisfactory since it is completely predictive. As suggested by Qian et al. **[6.1]**, predictions could be improved by including enthalpies of mixing and/or heat capacities in the objective function, at the risk of degrading VLE and LLE predictions. Some tests will be done in the near future.

As the main subject of this work is hydrate inhibition during transport, it must be pointed out that glycols are also hydrate inhibitors. Ethylene glycol is the most effective among all glycols and used mostly in the North Sea operations. To complete and cover as much as possible all systems encountered in natural gas transport, it is planned to add them to the model. However, after a non-exhaustive literature review, it seems that experimental data are limited.

To complete the model and enlarge its application to other industrial domains, parameters adjustment for the remaining groups with alcohols is still undergoing. In petrochemical industry, alcohols are used as solvents in extractive distillation to separate closely boiling hydrocarbons. Alcohol-water systems are present in separation of fusel oil from fermentation. In general, they present interesting properties, such as liquidlike density, low viscosity and high diffusivity. The multitude of applications of alcohols in the industry and the need of a predictive (as seen already for methane – alcohols systems and in Appendices A.3 to A.18, data can be limited.) model, emphasise the interest of adding these groups in the model.

It is known that cubic equations of state poorly predict liquid densities, because the co-volume is kept constant. But for liquid systems, the free space between molecules tends to reduce and in this case the role of the co-volume overcomes the one of the attractive parameter. It would be interesting to modify the co-volume by adding a mixing rule to the co-volum to improve LLE predictions. An additional binary interaction parameter (l_{ij}) must thus be defined: first, the influence of temperature must be evaluated. In the case of temperature dependence, there are two possibilities: or correlations are defined for each binary system considered or a group contribution method can be applied, so the model would still be predictive.

Finally, it has been seen that the temperature dependent binary interaction parameter can be used for different cubic equations of state and not only for the Peng-Robinson EoS. As for PR_2SRK, it would be interesting to develop a relationship between the GC-PR-CPA model and a group contribution method adapted to the SRK-CPA EoS. The relationship between the two binary interaction parameters relies on different hypothesis, and can be reduced to a constant at the end. However in the GC-PR-CPA model parameters for pure compounds have been re-adjusted. And hypothesis used must be checked for this equation of state. Right now, there is no simple and obvious relationship between both binary interaction parameters.

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APPENDICES

APPENDIX A.1. BINARY SYSTEMS CONTAINING WATER

Table A.1: Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with water

Components	References	Data rejected	Temperature range [K]	Pressure range [MPa]
Methane	[A1.1], [A1.2], [A1.3], [A1.4], [A1.5], [A1.6], [A1.7], [A1.8], [A1.9], [A1.10], [A1.11], [A1.12], [A1.13], [A1.14], [A1.15], [A1.16]		274– 623	0.1 – 108
Ethane	[A1.17], [A1.2], [A1.5], [A1.6], [A1.11], [A1.14], [A1.18], [A1.19], [A1.20], [A1.21], [A1.22], [A1.23], [A1.24], [A1.25], [A1.26]		259 – 444	0.05 – 685
Propane	[A1.27], [A1.28], [A1.29], [A1.11], [A1.14], [A1.19], [A1.24], [A1.30], [A1.31], [A1.32], [A1.33], [A1.34], [A1.26]		247 – 422	0.01 – 19
***n*-Butane**	[A1.33], [A1.35], [A1.11], [A1.14], [A1.36], [A1.23], [A1.24], [A1.26], [A1.30], [A1.31], [A1.32], [A1.37], [A1.38]	[A1.38], [A1.39]	273 – 511	0.1 – 69
***n*-Pentane**	[A1.26], [A1.40], [A1.41], [A1.23], [A1.42], [A1.43], [A1.44], [A1.45], [A1.46]	[A1.16], [A1.47], [A1.48]	273 – 625	0.02 – 71

Table A.1 (to be continued): Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with water

Components	**References**	**Data rejected**	**Temperature range [K]**	**Pressure range [MPa]**
***n*-Hexane**	[A1.26], [A1.49], [A1.42], [A1.43], [A1.44], [A1.45], [A1.50], [A1.51], [A1.52], [A1.53], [A1.54]	[A1.55], [A1.56]	273 – 671	0.01 – 0.8
***n*-Heptane**	[A1.23], [A1.42], [A1.44], [A1.57]		273 – 373	0.1
***n*-Octane**	[A1.42], [A1.43], [A1.44], [A1.58]		273 – 433	0.1
***n*-Nonane**	[A1.59], [A1.44], [A1.45], [A1.60]		288 – 410	0.1
***n*-Decane**	[A1.61], [A1.62], [A1.63], [A1.64]		293 – 542	0.1 – 1
***n*-Undecane**	[A1.60], [A1.65]		298 – 298	0.1
***n*-Dodecane**	[A1.62], [A1.65], [A1.66], [A1.67]		298 – 425	0.1 – 5
***n*-Tetradecane**	[A1.52], [A1.66], [A1.67]		298 – 473	0.1 – 5
***n*-Hexadecane**	[A1.62], [A1.66], [A1.67], [A1.68], [A1.64]		298 – 526	0.1 – 5
***n*-Octadecane**	[A1.66]		298	0.1
***n*-Eicosane**	[A1.66], [A1.67]		298 – 473	0.1 – 5
***n*-Octacosane**	[A1.64]		429 – 519	0.15 – 0.25
***i*-Butane**	[A1.11], [A1.23], [A1.31]		278 – 318	0.1
***i*-Pentane**	[A1.40], [A1.43], [A1.42], [A1.45]		273 – 333	0.1

Table A.1 (to be continued): Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with water

Components	References	Data rejected	Temperature range [K]	Pressure range [MPa]
***2,3*-Dimethylbutane**	[A1.49], [A1.43], [A1.42], [A1.45]		273 – 423	0.1 – 0.7
***2,2*-Dimethylpropane**	[A1.42]		298	0.1
***2,2*-Dimethylbutane**	[A1.42], [A1.43], [A1.45], [A1.49]		273 – 298	0.1
***2,2*-Dimethylpentane**	[A1.45]		298	0.1
***3,3*-Dimethylpentane**	[A1.45]		298 – 423	0.1
Cyclopentane	[A1.40], [A1.42]	[A1.48]	278 – 373	0.1
Cyclohexane	[A1.69], [A1.11], [A1.23], [A1.45], [A1.50], [A1.51], [A1.70], [A1.71], [A1.72], [A1.73]	[A1.48], [A1.56]	274 – 425	0.1
Cycloheptane	[A1.42]		298	0.1
Cyclooctane	[A1.42]		298	0.1
Methylcyclopentane	[A1.23], [A1.42], [A1.45], [A1.69], [A1.74]		298 – 487	0.1
Methylcyclohexane	[A1.23], [A1.42], [A1.57]		298 – 423	0.1
Ethylcyclopentane	[A1.74]		344 – 476	0.1

Table A.1 (to be continued): Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with water

Components	**References**	**Data rejected**	**Temperature range [K]**	**Pressure range [MPa]**
Benzene	[A1.11], [A1.14], [A1.43], [A1.45], [A1.51], [A1.54], [A1.62], [A1.70], [A1.71], [A1.75], [A1.76], [A1.77], [A1.78], [A1.79], [A1.80]	[A1.47], [A1.48], [A1.81], [A1.82], [A1.83]	260 – 473	0.1 – 81
Toluene	[A1.57], [A1.76], [A1.11], [A1.14], [A1.45], [A1.43], [A1.51], [A1.54], [A1.66], [A1.73], [A1.78], [A1.84], [A1.85]	[A1.48], [A1.75], [A1.81], [A1.82]	273 – 583	0.1 – 61
Ethylbenzene	[A1.76], [A1.86], [A1.11], [A1.14], [A1.43], [A1.45], [A1.51], [A1.54], [A1.66], [A1.73], [A1.78], [A1.85], [A1.87]	[A1.75], [A1.81], [A1.82]	273 – 373	0.1
***o*-Xylene**	[A1.86], [A1.11], [A1.43], [A1.45], [A1.66], [A1.82], [A1.84]		273 – 318	0.1
***m*-Xylene**	[A1.86], [A1.43], [A1.45], [A1.66], [A1.75], [A1.82], [A1.84]		273 – 343	0.1
***p*-Xylene**	[A1.86], [A1.43], [A1.45], [A1.66], [A1.75], [A1.82], [A1.84]		273 – 363	0.1

Table A.1 (to be continued): Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with water

Components	References	Data rejected	Temperature range [K]	Pressure range [MPa]
Carbon dioxide	[A1.88], [A1.14], [A1.89], [A1.90], [A1.91], [A1.92], [A1.93], [A1.94], [A1.95], [A1.96], [A1.97], [A1.98], [A1.99], [A1.100], [A1.101], [A1.102], [A1.103], [A1.104], [A1.105]		273 – 607	0.008 – 80
Nitrogen	[A1.106], [A1.12], [A1.14], [A1.16], [A1.25], [A1.107], [A1.108], [A1.109], [A1.110], [A1.111], [A1.112], [A1.113], [A1.114], [A1.115], [A1.116], [A1.117]		273 – 589	0.1 – 61
Hydrogen sulphide	[A1.16], [A1.118], [A1.119], [A1.120], [A1.121], [A1.122], [A1.123], [A1.124], [A1.125], [A1.126], [A1.127]		273 – 594	0.04 – 21

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APPENDIX A.2. BINARY SYSTEMS CONTAINING METHANOL

Table A.2: Sources of vapour-liquid and liquid-liquid equilibrium data for binary systems with methanol

Components	**VLE**	**LLE**	**Data rejected**	**Temperature range**	**Pressure range [MPa]**
Methane	[A2.1], [A2.2], [A2.3], [A2.4], [A2.5], [A2.6], [A2.7], [A2.8]			183 – 472	0.1 – 250
Ethane	[A2.4], [A2.9], [A2.10], [A2.6], [A2.11], [A2.12], [A2.13], [A2.14], [A2.15], [A2.16]		[A2.11], [A2.16], [A2.17]	184 – 373	0.06 – 7
Propane	[A2.18], [A2.19], [A2.20], [A2.21], [A2.22]			293 – 474	0.06 – 9
***n*-Butane**	[A2.23], [A2.20], [A2.24], [A2.21], [A2.25], [A2.26], [A2.22], [A2.27]	[A2.28]	[A2.28]	264 – 470	0.06 – 140
***n*-Pentane**	[A2.29], [A2.30], [A2.31], [A2.32]	[A2.33], [A2.28]	[A2.28], [A2.33], [A2.34]	270 – 423	0.05 – 140
***n*-Hexane**	[A2.32], [A2.35],[A2.36], [A2.37], [A2.38], [A2.39], [A2.40], [A2.41], [A2.42], [A2.43]	[A2.44], [A2.45], [A2.46], [A2.47], [A2.48], [A2.49], [A2.34], [A2.50], [A2.51]	[A2.36], [A2.38], [A2.52] [A2.44], [A2.49], [A2.34], [A2.50]	255 – 513	0.02 – 151
***n*-Heptane**	[A2.36], [A2.38], [A2.53], [A2.54]	[A2.55], [A2.33], [A2.56], [A2.57], [A2.47], [A2.48], [A2.58], [A2.34], [A2.51], [A2.59]	[A2.36], [A2.38], [A2.53], [A2.33], [A2.56]	268 – 540	0.01 – 151

Table A.2 (to be continued): Sources of vapour-liquid and liquid-liquid equilibrium data for binary systems with methanol

Components	**VLE**	**LLE**	**Data rejected**	**Temperature range [K]**	**Pressure range [MPa]**
***n*-Octane**		[A2.60], [A2.56], [A2.59]	[A2.36], [A2.56], [A2.57], [A2.48], [A2.34]	278 – 372	0.1 – 151
***n*-Nonane**	[A2.36]		[A2.56], [A2.57], [A2.60], [A2.61], [A2.49], [A2.33], [A2.62]	416 – 537	1 – 7.5
***n*-Decane**	[A2.36]		[A2.56], [A2.57], [A2.62], [A2.61], [A2.63], [A2.49],	422 – 540	1 – 8
***n*-Undecane**			[A2.33], [A2.57], [A2.62], [A2.63]	278 – 376	0.1
***n*-Dodecane**	[A2.36]	[A2.57], [A2.62], [A2.63]		278 – 536	0.1 – 9
***n*-Tetradecane**			[A2.36], [A2.65]	298 – 535	0.1 – 9
***n*-Hexadecane**	[A2.66]			298 – 318	5.10^{-4} – 0.04
***i*-Butane**	[A2.67], [A2.68], [A2.69], [A2.20]			273 – 423	0.03 – 5
***i*-Pentane**	[A2.70]			297 – 304	0.1
2,3-Dimethylbutane	[A2.71], [A2.72], [A2.73]	[A2.52]		283 – 334	0.1
2,2-Dimethylbutane		[A2.52]		275 – 296	0.1

Table A.2 (to be continued): Sources of vapour-liquid and liquid-liquid equilibrium data for binary systems with methanol

Components	**VLE**	**LLE**	**Data rejected**	**Temperature range [K]**	**Pressure range [MPa]**
Cyclohexane	[A2.74], [A2.75], [A2.76], [A2.39],	[A2.52], [A2.58], [A2.77], [A2.78], [A2.79], [A2.80], [A2.81], [A2.82], [A2.46], [A2.83]	[A2.81], [A2.84], [A2.85]	278 – 333	0.01 – 14
Cycloheptane		[A2.44]		290 – 340	0.1
Cyclooctane		[A2.44]		266 – 358	0.1
Methyl-cyclopentane	[A2.86], [A2.87]	[A2.88]		296 – 345	0.1 – 120
Methylcyclo-hexane	[A2.53],	[A2.89], [A2.90]		298 – 318	0.03 – 0.1
Benzene	[A2.91], [A2.92], [A2.93], [A2.94], [A2.95], [A2.96], [A2.97], [A2.39], [A2.98], [A2.87], [A2.99], [A2.53], [A2.100], [A2.101], [A2.102], [A2.103], [A2.104]		[A2.104]	298 – 353	0.02 – 0.1
Toluene	[A2.100], [A2.105], [A2.106], [A2.53], [A2.107], [A2.108]			313 – 384	0.008 – 0.1
Ethylbenzene	[A2.109], [A2.109]			338 – 407	0.1
***o*-Xylene**	[A2.110], [A2.111]			336 – 415	0.1
***p*-Xylene**	[A2.112], [A2.100]			313 – 409	0.003 – 0.1

Table A.2 (to be continued): Sources of vapour-liquid and liquid-liquid equilibrium data for binary systems with methanol

Components	**VLE**	**LLE**	**Data rejected**	**Temperature range [K]**	**Pressure range [MPa]**
Carbon dioxide	[A2.113], [A2.114], [A2.115], [A2.116], [A2.117], [A2.118], [A2.119], [A2.120], [A2.121], [A2.122], [A2.123], [A2.124], [A2.125], [A2.126], [A2.127], [A2.128], [A2.129], [A2.3]		[A2.130]	213 – 478	0.1 – 18.5
Nitrogen	[A2.3], [A2.131], [A2.8], [A2.6], [A2.132], [A2.133], [A2.12], [A2.134], [A2.125], [A2.5], [A2.135]			213 – 373	0.1 – 108
Hydrogen sulphide	[A2.136], [A2.137], [A2.138], [A2.124]			223 – 448	2.10^{-4} – 11
Hydrogen	[A2.139], [A2.140], [A2.134], [A2.141], [A2.3]		[A2.130], [A2.142]	213 – 477	0.04 – 110
Ethylene	[A2.143], [A2.144], [A2.12], [A2.145], [A2.146], [A2.147]	[A2.145], [A2.146]	[A2.145], [A2.143], [A2.147]	240 – 432	0.1 – 15.5
Propylene	[A2.148]			298	0.5 – 2
Water	[A2.149], [A2.150], [A2.151], [A2.152], [A2.153], [A2.154], [A2.155], [A2.156], [A2.157], [A2.158], [A2.159], [A2.160], [A2.161], [A2.162], [A2.163], [A2.164], [A2.165], [A2.166], [A2.167], [A2.168]		[A2.169]	308 – 442	0.006 – 2

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APPENDIX A.3. BINARY SYSTEMS CONTAINING ETHANOL

Table A.3: Sources of vapour-liquid and liquid-liquid equilibrium data for binary systems with ethanol

Components	VLE	LLE	Data rejected	Temperature range [K]	Pressure range [MPa]
Methane	[A3.1], [A3.2], [A3.3], [A3.4]			280 – 498	0.5 – 36
Ethane	[A3.3], [A3.1], [A3.5], [A3.6]			298 – 498	0.3 – 12
Propane	[A3.7], [A3.8], [A3.9], [A3.10], [A3.11], [A3.12]			273 – 500	0.03 – 6
***n*-Butane**	[A3.13], [A3.14], [A3.15], [A3.16], [A3.17], [A3.18]			283 – 500	0.006 – 9
***n*-Pentane**	[A3.19], [A3.20], [A3.21], [A3.22]			303 – 500	0.03 – 6
***n*-Hexane**	[A3.23], [A3.24], [A3.25], [A3.26], [A3.27], [A3.28], [A3.29], [A3.30], [A3.31], [A3.32], [A3.33]			298 – 508	0.01 – 6
***n*-Heptane**	[A3.31], [A3.34], [A3.35], [A3.36], [A3.37], [A3.38], [A3.39], [A3.40], [A3.41], [A3.42], [A3.43]			303 – 523	0.004 – 6
***n*-Octane**	[A3.31], [A3.44], [A3.45], [A3.46]			308 – 359	0.004 – 0.
***n*-Nonane**	[A3.36]			343	0.006 – 0.07
***n*-Decane**	[A3.6]	[A3.47]		307 – 447	0.1
***n*-Undecane**	[A3.48]			333 – 353	0.0006 – 0.1

Table A.3 (to be continued): Sources of vapour-liquid and liquid-liquid equilibrium data for binary systems with ethanol

Components	**VLE**	**LLE**	**Data rejected**	**Temperature range [K]**	**Pressure range [MPa]**
***n*-Dodecane**		[A3.49], [A3.50]	[A3.50]	271 – 309	0.1 – 120
***n*-Tridecane**		[A3.50]		294 – 297	0.1
***n*-Tetradecane**		[A3.49], [A3.51]	[A3.49]	280 – 331	0.1 – 120
***n*-Hexadecane**	[A3.52]	[A3.49], [A3.51], [A3.53], [A3.52]	[A3.49], [A3.51], [A3.53], [A3.52]	290 – 348	0.004 – 120
***n*-Octadecane**	[A3.54]	[A3.55]		283. – 337	0.1
***n*-Nonadecane**	[A3.54]			283 – 304	0.1
***i*-Butane**	[A3.56], [A3.7]			309 – 364	0.02 – 2
***2,3*-Dimethylbutane**	[A3.57]			325 – 343	0.1
Cyclopentane	[A3.58]			323 – 374	0.1 – 0.5
Cyclohexane	[A3.59], [A3.60], [A3.61]		[A3.32]	278 – 338	0.002 – 0.1
Methylcyclopentane	[A3.30]			333 – 349	0.1
Methylcyclohexane	[A3.62]			345 – 369	0.1
Benzene	[A3.63], [A3.64], [A3.65], [A3.66], [A3.33], [A3.67], [A3.29], [A3.68], [A3.32], [A3.69], [A3.70], [A3.71]			294 – 347	0.008 – 0.1
Toluene	[A3.72], [A3.66], [A3.73], [A3.74], [A3.75], [A3.76], [A3.77]			286 – 383	0.004 – 0.1

Table A.3 (to be continued): Sources of vapour-liquid and liquid-liquid equilibrium data for binary systems with ethanol

Components	VLE	LLE	Data rejected	Temperature range [K]	Pressure range [MPa]
Ethylbenzene	[A3.6], [A3.78]			350 – 409	0.1
***m*-Xylene**	[A3.79], [A3.80]			298 – 408	0.004 – 0.1
***o*-Xylene**	[A3.81], [A3.82]			308 – 410	0.003 – 0.1
***p*-Xylene**	[A3.79], [A3.66], [A3.62]			313 – 409	0.003 – 0.1
Ethylene	[A3.83]	[A3.83]		284	1 – 5
Propylene	[A3.84]			331 – 368	1 – 5
Carbon dioxide	[A3.85], [A3.86], [A3.3], [A3.87], [A3.88], [A3.89], [A3.90], [A3.91], [A3.92], [A3.93], [A3.94], [A3.95], [A3.96], [A3.97], [A3.98], [A3.99], [A3.4], [A3.100], [A3.101], [A3.102], [A3.103], [A3.104], [A3.105]			283 – 496	0.09 – 15
Nitrogen	[A3.106], [A3.107], [A3.108], [A3.109], [A3.110], [A3.4]			298 – 398	0.1 – 10
Hydrogen	[A3.1], [A3.109], [A3.111], [A3.112]			213 – 508	0.1 – 34
Methanol	[A3.113], [A3.63], [A3.114], [A3.115]			303 – 351	0.01 – 0.1

Table A.3 (to be continued): Sources of vapour-liquid and liquid-liquid equilibrium data for binary systems with ethanol

Components	**VLE**	**LLE**	**Data rejected**	**Temperature range [K]**	**Pressure range [MPa]**
Water	[A3.116], [A3.117], [A3.118], [A3.119], [A3.120], [A3.121], [A3.122], [A3.123], [A3.124], [A3.99], [A3.125], [A3.126], [A3.127], [A3.128], [A3.129], [A3.130], [A3.131], [A3.132], [A3.133], [A3.134], [A3.135], [A3.136], [A3.137], [A3.138], [A3.139], [A3.140], [A3.141], [A3.142], [A3.143], [A3.144], [A3.145]			283 – 548	0.002 – 10

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APPENDIX A.4. BINARY SYSTEMS CONTAINING N-PROPANOL

Table A.4: Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with n-propanol

Components	References	Data rejected	Temperature range [K]	Pressure range [MPa]
Methane	[A4.1]		313 – 333	1 – 10
Ethane	[A4.2], [A4.3], [A4.4], [A4.5], [A4.4]	[A4.3], [A4.5]	313 – 349	0.1 – 9.5
Propane	[A4.5], [A4.6]		318 – 393	0.45 – 4
***n*-Butane**	[A4.7], [A4.8], [A4.9],		283 – 523	0.02 – 5
***n*-Pentane**	[A4.10], [A4.11]		313 – 513	0.007 – 5
***n*-Hexane**	[A4.12], [A4.13], [A4.14], [A4.15], [A4.16], [A4.17], [A4.18], [A4.19]		298 – 369	0.003 – 0.15
***n*-Heptane**	[A4.20], [A4.21], [A4.22], [A4.23], [A4.24], [A4.25], [A4.26], [A4.16], [A4.27], [A4.28], [A4.29], [A4.30]		278 – 523	0.002 – 4
***n*-Octane**	[A4.27], [A4.31], [A4.32]		313 – 400	0.004 – 0.1
***n*-Nonane**	[A4.33]		298	0.002 – 0.003
***n*-Decane**	[A4.34], [A4.35]		363 – 366	0.05 – 0.07
***i*-Butane**	[A4.36], [A4.9]		318 – 364	0.01 – 2
Cyclohexane	[A4.14], [A4.37], [A4.38], [A4.39], [A4.40], [A4.41]		298 – 370	0.003 – 0.1
Methyl-cyclohexane	[A4.42], [A4.43], [A4.44]		333 – 374	0.03 – 0.1

Table A.4 (to be continued): Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with n-propanol

Components	References	Data rejected	Temperature range [K]	Pressure range [MPa]
Benzene	[A4.45], [A4.46], [A4.47], [A4.48], [A4.12], [A4.20], [A4.14], [A4.37], [A4.49], [A4.39], [A4.40], [A4.50], [A4.51]		298 – 370	0.003 – 0.1
Toluene	[A4.49], [A4.39]		298 – 313	0.003 – 0.01
Ethylbenzene	[A4.52]		369 – 407	0.1
***o*-Xylene**	[A4.39]		298	0.0009 – 0.003
***m*-Xylene**	[A4.39]		298	0.001 – 0.003
***p*-Xylene**	[A4.39], [A4.53], [A4.49], [A4.54], [A4.55]		298 – 494	0.001 – 3
Carbon dioxide	[A4.3], [A4.56], [A4.57], [A4.58], [A4.59]		298 – 427	0.5 – 16
Nitrogen	[A4.60], [A4.61]		298 – 398	0.003 – 10
Hydrogen	[A4.62], [A4.63]		291 – 514	1 – 10
Water	[A4.64], [A4.34], [A4.65], [A4.66], [A4.67], [A4.68], [A4.69], [A4.70], [A4.71], [A4.72]	[A4.66]	273 – 373	0.0007 – 0.1
Methanol	[A4.73], [A4.74], [A4.75]		333 – 370	0.02 – 0.1
Ethanol	[A4.76], [A4.28], [A4.77]		298 – 313	0.003 – 0.02

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APPENDIX A.5. BINARY SYSTEMS CONTAINING N-BUTANOL

Table A.5: Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with n-butanol

Components	References	Data rejected	Temperature range [K]	Pressure range [MPa]
Ethane	[A5.1], [A5.2], [A5.3], [A5.1]	[A5.2]	298 – 314	0.0002 – 5.5
***n*-Butane**	[A5.4], [A5.5], [A5.6], [A5.7]		283 – 521	0.04 – 5
***n*-Pentane**	[A5.8], [A5.9]		303 – 513	0.001 – 4
***n*-Hexane**	[A5.10], [A5.11], [A5.12], [A5.13], [A5.14], [A5.15]		283 – 389	0.0003 – 0.1
***n*-Heptane**	[A5.16], [A5.17], [A5.18], [A5.19], [A5.20], [A5.21], [A5.22], [A5.23]		303 – 434	0.001 – 0.5
***n*-Octane**	[A5.24], [A5.25], [A5.26], [A5.27], [A5.28]		283 – 400	0.0004 – 0.1
***n*-Nonane**	[A5.11], [A5.29]		323 – 371	0.005 – 0.05
***n*-Decane**	[A5.30], [A5.24], [A5.31]		358 – 388	0.005 – 0.09
***i*-Butane**	[A5.4]		298 – 323	0.1
Cyclohexane	[A5.32], [A5.33], [A5.19], [A5.34]		318 – 389	0.003 – 0.2
Methylcyclohexane	[A5.35], [A5.36], [A5.37], [A5.38]		333 – 391	0.01 – 0.1
Ethylene	[A5.39]		264 – 343	0.1
Propylene	[A5.40]		298 – 343	0.2 – 2

Table A.5 (to be continued): Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with n-butanol

Components	**References**	**Data rejected**	**Temperature range [K]**	**Pressure range [MPa]**
Benzene	[A5.41], [A5.42], [A5.43], [A5.44], [A5.45], [A5.46], [A5.47], [A5.48], [A5.49]		298 – 425	0.0008 – 0.3
Toluene	[A5.50], [A5.51], [A5.36], [A5.45], [A5.52], [A5.48]		308 – 391	0.003 – 0.1
Ethylbenzene	[A5.53], [A5.54]		337 – 407	0.01 – 0.1
***o*-Xylene**	[A5.48]		308.2	0.001 – 0.003
***m*-Xylene**	[A5.55], [A5.48]		308 – 408.0	0.002 – 0.1
***p*-Xylene**	[A5.56], [A5.45], [A5.57], [A5.48]		308 – 412	0.002 – 0.1
Carbon dioxide	[A5.58], [A5.59], [A5.60], [A5.61], [A5.62], [A5.63], [A5.64], [A5.65], [A5.66], [A5.67], [A5.68]		293 – 430	0.1 – 17
Hydrogen	[A5.69], [A5.70]		291 – 525	1.5 – 9
Hydrogen sulphide	[A5.71]		263 – 333	0.1

Table A.5 (to be continued): Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with n-butanol

Components	**References**	**Data rejected**	**Temperature range [K]**	**Pressure range [MPa]**
Water	[A5.72], [A5.73], [A5.74], [A5.75], [A5.76], [A5.77], [A5.78], [A5.79], [A5.19], [A5.80], [A5.81], [A5.82], [A5.83], [A5.84], [A5.85], [A5.86], [A5.87], [A5.88], [A5.89], [A5.90], [A5.91], [A5.92], [A5.93], [A5.94], [A5.95], [A5.96], [A5.97], [A5.98], [A5.99], [A5.100], [A5.101], [A5.102], [A5.103], [A5.104], [A5.105], [A5.106], [A5.107], [A5.108], [A5.109], [A5.110], [A5.111], [A5.112], [A5.113], [A5.114], [A5.84]	[A5.72], [A5.73], [A5.74], [A5.75], [A5.76], [A5.77], [A5.78], [A5.79], [A5.19], [A5.81], [A5.83]	255 – 401	0.0009 – 248
Methanol	[A5.115], [A5.116], [A5.117], [A5.118]		298 – 559	0.0009 – 7
Ethanol	[A5.119], [A5.120], [A5.121], [A5.28]		308 – 391	0.1
***n*-Propanol**	[A5.122]		337 – 374	0.02 – 0.1
***i*-Propanol**	[A5.123]		325 – 385	0.03 – 0.1

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APPENDIX A.6. BINARY SYSTEMS CONTAINING N-PENTANOL

Table A.6: Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with n-pentanol

Components	References	Data rejected	Temperature range [K]	Pressure range [MPa]
***n*-Pentane**	[A6.1]		303	0.0004 – 0.08
***n*-Hexane**	[A6.1], [A6.2], [A6.3], [A6.4]		298 – 343	0.0003 – 0.1
***n*-Heptane**	[A6.5], [A6.6], [A6.7], [A6.8]		313 – 417	0.0009 – 0.1
***n*-Nonane**	[A6.9]		410 – 424	0.1
Cyclohexane	[A6.10], [A6.4]		315 – 436	0.03 – 0.04
Ethylene	[A6.11]		343 – 373	2.5 – 16
Benzene	[A6.12]		313	0.0009 – 0.03
Toluene	[A6.13]		303 -390	0.0006 – 0.1
Ethylbenzene	[A6.14]		397 – 407	0.1
***p*-Xylene**	[A6.15]		404 – 412	0.1
Carbon dioxide	[A6.16], [A6.17], [A6.18]		283 – 427	2 – 19
Water	[A6.19], [A6.20], [A6.21], [A6.22], [A6.23], [A6.24], [A6.25], [A6.26], [A6.27], [A6.28], [A6.29], [A6.30], [A6.31], [A6.32], [A6.33], [A6.34], [A6.35], [A6.36], [A6.37], [A6.38], [A6.39], [A6.40]	[A6.19]	273 – 463	0.1 – 90
Methanol	[A6.41], [A6.42], [A6.43]		313 – 410	0.0009 – 0.1

Table A.6: Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with n-pentanol

Components	References	Data rejected	Temperature range [K]	Pressure range [MPa]
Ethanol	[A6.44], [A6.5]		334 – 417	0.05 – 0.15
***n*-Propanol**	[A6.45], [A6.46], [A6.47]		313 – 411	0.0009 – 0.1
***i*-Propanol**	[A6.45]		313	0.0009 – 0.01

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APPENDIX A.7. BINARY SYSTEMS CONTAINING N-HEXANOL

Table A.7: Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with n-hexanol

Components	References	Data rejected	Temperature range [K]	Pressure range [MPa]
***n*-Hexane**	[A7.1], [A7.2], [A7.3]		293 – 422	6.10^{-5} – 0.1
***n*-Heptane**	[A7.1]		372 – 428	0.1
***p*-xylene**	[A7.4]		411 – 429	0.1
Carbon dioxide	[A7.5], [A7.6], [A7.7], [A7.5]	[A7.5]	218 – 433	0.5 – 20
Water	[A7.8], [A7.9], [A7.10], [A7.11], [A7.12], [A7.13], [A7.14], [A7.15], [A7.16], [A7.17], [A7.18], [A7.19], [A7.20], [A7.21], [A7.22], [A7.23], [A7.24]		273 – 493	0.1

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APPENDIX A.8. BINARY SYSTEMS CONTAINING N-HEPTANOL

Table A.8: Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with n-heptanol

Components	References	Temperature range [K]	Pressure range [MPa]
Methane	[A8.1]	298	0.1
Ethane	[A8.1]	298	0.1
***n*-Decane**	[A8.2]	342 – 439	0.003 – 0.1
Toluene	[A8.3]	384 – 447	0.1
Cyclohexane	[A8.4]	318 – 476	0.03 – 0.4
Ethylene	[A8.1]	298	0.1
Carbon dioxide	[A8.5]	375 – 432	4.0 – 21
Water	[A8.6], [A8.7], [A8.8], [A8.9], [A8.10], [A8.11]	273 – 363	0.1

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APPENDIX A.9. BINARY SYSTEMS CONTAINING N-OCTANOL

Table A.9: Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with n-octanol

Components	References	Data rejected	Temperature range [K]	Pressure range [MPa]
Ethane	[A9.1], [A9.2]		289 – 338	2 – 11
***n*-Hexane**	[A9.3]		313	0.009 – 0.04
***n*-Heptane**	[A9.4]		293	5.10^{-4} – 0.005
***n*-Octane**	[A9.5]		373 – 383	0.003 – 0.06
***n*-Decane**	[A9.6]		243 – 383	0.003 – 0.1
Cyclohexane	[A9.7]		321 – 485	0.03 – 0.4
Ethylene	[A9.2]		318 – 338	3 – 18
Carbon dioxide	[A9.2], [A9.8], [A9.9], [A9.10], [A9.11]	[A9.2], [A9.8]	250 – 453	1 – 19
Nitrogen	[A9.12], [A9.13]		273 – 453	1 – 10
Hydrogen	[A9.12], [A9.14]		273 – 318	0.7 – 8.5
Water	[A9.15], [A9.16], [A9.17], [A9.18], [A9.19], [A9.20], [A9.21], [A9.22], [A9.23], [A9.24], [A9.25]		283 – 559	0.1 – 10
Methanol	[A9.26]		338 – 468	0.1
Ethanol	[A9.26]		352 – 468	0.1
***n*-Hexanol**	[A9.27]		356 – 391	0.004 – 0.01

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APPENDIX A.10. BINARY SYSTEMS CONTAINING N-NONANOL

Table A.10: Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with n-nonanol

Components	**References**	**Data rejected**	**Temperature range [K]**	**Pressure range [MPa]**
***m*-Xylene**	[A10.1]		415 – 452	0.1
***p*-Xylene**	[A10.1]		414 – 451	0.1
Carbon dioxide	[A10.2]		303	11 – 34
Water	[A10.3], [A10.4]		273 – 363	0.1

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APPENDIX A.11. BINARY SYSTEMS CONTAINING N-DECANOL

Table A.11: Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with n-decanol

Components	References	Data rejected	Temperature range [K]	Pressure range [MPa]
Ethane	[A11.1], [A11.2], [A11.3]	[A11.1], [A11.2]	275 – 307	2.5 – 5
Propane	[A11.4]		378 – 408	4 – 7
***n*-Hexane**	[A11.5]		283 – 333	0.003 – 0.07
Carbon dioxide	[A11.6], [A11.7], [A11.8], [A11.9]	[A11.6]	271 – 453	1 – 19
Nitrogen	[A11.10]		333 – 453	1 – 10
Water	[A11.11], [A11.12], [A11.13], [A11.14], [A11.15]		292 – 590	0.1 – 90
Methanol	[A11.16]		293 – 323	2.10^{-6} – 0.06
Ethanol	[A11.16]		293 – 323	2.10^{-6} – 0.03
***n*-Propanol**	[A11.17]		293 – 323	2.10^{-6} – 0.01
***2*-Propanol**	[A11.18]		293 – 323	2.10^{-6} – 0.02

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APPENDIX A.12. BINARY SYSTEMS CONTAINING 2-PROPANOL

Table A.12: Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with 2-propanol

Components	References	Data rejected	Temperature range [K]	Pressure range [MPa]
Ethane	[A12.1]		308 – 313	2 – 5
Propane	[A12.2], [A12.3]		273 – 353	0.001 – 3
***n*-Butane**	[A12.2], [A12.4], [A12.5]		298 – 365	0.01 – 1
***n*-Hexane**	[A12.6], [A12.7], [A12.8], [A12.9], [A12.10], [A12.11], [A12.12]		303 – 503	0.008 – 5
***n*-Heptane**	[A12.13], [A12.14], [A12.7], [A12.15], [A12.16], [A12.17], [A12.18], [A12.19], [A12.20], [A12.21]		298 – 523	0.008 – 5
***n*-Octane**	[A12.22], [A12.23], [A12.24]		338 – 400	0.02 – 0.1
***n*-Decane**	[A12.25]		363	0.1
***i*-Butane**	[A12.2], [A12.26], [A12.27]		298 – 390	0.01 – 3
Cyclohexane	[A12.28], [A12.29], [A12.30], [A12.31], [A12.32], [A12.33], [A12.34],		298 – 350	0.006 – 0.1
Methyl-cyclohexane	[A12.29], [A12.31], [A12.35]		323 – 374	0.03 – 0.1
Ethylene	[A12.36], [A12.37]		273 – 323	0.1 – 5
Propylene	[A12.3], [A12.38]		298 – 370	0.2 – 4

Table A.12 (to be continued): Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with 2-propanol

Components	**References**	**Data rejected**	**Temperature range [K]**	**Pressure range [MPa]**
Benzene	[A12.39], [A12.40], [A12.29], [A12.31], [A12.41], [A12.42], [A12.43], [A12.44]		298 – 355	0.006 – 0.1
Toluene	[A12.45], [A12.46], [A12.43]		298 – 377	0.004 – 0.1
Ethylbenzene	[A12.47], [A12.48]		354 – 409	0.1
***m*-Xylene**	[A12.43]		298	0.001 – 0.006
***o*-Xylene**	[A12.43]		298	9.10^{-4} – 0.006
***p*-Xylene**	[A12.43], [A12.47]		298 – 412	0.001 – 0.1
Carbon dioxide	[A12.49], [A12.50], [A12.51], [A12.52], [A12.53], [A12.54], [A12.55], [A12.56], [A12.57]		293 – 444	0.7 – 14
Nitrogen	[A12.58]		333 – 393	2 – 10
Water	[A12.59], [A12.60], [A12.61], [A12.62], [A12.30], [A12.63], [A12.64], [A12.65], [A12.66], [A12.67], [A12.68], [A12.41], [A12.69], [A12.70], [A12.71], [A12.72], [A12.73], [A12.74], [A12.75], [A12.76], [A12.77], [A12.78], [A12.79], [A12.80]	[A12.61]	288 – 584	0.01 – 12
Methanol	[A12.81], [A12.82], [A12.83], [A12.84], [A12.85]		328 – 356	0.03 – 0.1

Table A.12 (to be continued): Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with 2-propanol

Components	References	Data rejected	Temperature range [K]	Pressure range [MPa]
Ethanol	[A12.81], [A12.86], [A12.17], [A12.87]		303 – 356	0.008 – 0.1
***n*-Propanol**	[A12.81], [A12.88], [A12.89], [A12.90], [A12.91], [A12.92]		298 – 371	0.003 – 0.1

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APPENDIX A.13. BINARY SYSTEMS CONTAINING *2*-BUTANOL

Table A.13: Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with 2-butanol

Components	References	Data rejected	Temperature range [K]	Pressure range [MPa]
Methane	[A13.1]		263 – 303	0.1
Ethane	[A13.1]		263 – 303	0.1
***n*-Propane**	[A13.2]		328 – 368	1.0 – 4
***n*-Butane**	[A13.3], [A13.4]		323 – 365	0.01 – 1
***n*-Pentane**	[A13.5], [A13.6]		303 – 513	0.003 – 4
***n*-Hexane**	[A13.7], [A13.8], [A13.9], [A13.10], [A13.11], [A13.12]		298 – 371	0.002 – 0.2
***n*-Heptane**	[A13.13], [A13.14], [A13.15], [A13.16], [A13.17]		303 – 372	0.003 – 0.1
***n*-Octane**	[A13.18], [A13.19]		358 – 400	0.03 – 0.1
***i*-Butane**	[A13.20]		313	0.006 – 0.5
Cyclohexane	[A13.21], [A13.15], [A13.8], [A13.22], [A13.23]		318 – 373	0.008 – 0.1
Methyl-cyclohexane	[A13.24], [A13.25]		333 – 374	0.02 – 0.1
Ethylene	[A13.1]		263 – 303	0.1
Propylene	[A13.2]		333 – 368	1 – 4
Benzene	[A13.26], [A13.27], [A13.28], [A13.29], [A13.30]		298 – 318	0.002 – 0.03

Table A.13 (to be continued): Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with 2-butanol

Components	**References**	**Data rejected**	**Temperature range [K]**	**Pressure range [MPa]**
Toluene	[A13.29]		308	0.006 – 0.01
Ethylbenzene	[A13.31]		370 – 407	0.01
***m*-Xylene**	[A13.32], [A13.33], [A13.29]		308 – 409	0.002 – 0.1
***o*-Xylene**	[A13.29]		308	0.002 – 0.006
***p*-Xylene**	[A13.29], [A13.32]		308 – 408	0.003 – 0.09
Carbon dioxide	[A13.1], [A13.34], [A13.35], [A13.36], [A13.37]		294 – 532	0.1 – 15
Nitrogen	[A13.1], [A13.38]		263 – 393	0.1 – 10
Hydrogen	[A13.1]		263 – 303	0.1
Water	[A13.39], [A13.40], [A13.41], [A13.42], [A13.43], [A13.44], [A13.45], [A13.46], [A13.47], [A13.48], [A13.49], [A13.50], [A13.51], [A13.52], [A13.53], [A13.54], [A13.55], [A13.43], [A13.56], [A13.57], [A13.58], [A13.59]	[A13.40]	214 – 573	2.10^{-4} – 11
Methanol	[A13.60], [A13.5]		298 – 303	0.002 – 0.02
Ethanol	[A13.61]		352 – 373	0.1
***2*-Propanol**	[A13.62]		356 – 371	0.1
***n*-Butanol**	[A13.63], [A13.64], [A13.65], [A13.15]		313 – 390	0.003 – 0.1

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APPENDIX A.14. BINARY SYSTEMS CONTAINING *2*-PENTANOL

Table A.14: Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with 2-pentanol

Components	References	Data rejected	Temperature range [K]	Pressure range [MPa]
***n*-Heptane**	[A14.1], [A14.2]		313 – 368	0.002 – 0.1
Carbon dioxide	[A14.3], [A14.4]		313 – 432	1 – 16
Nitrogen	[A14.5]		333 – 393	2 – 10
Water	[A14.6], [A14.7], [A14.8], [A14.9], [A14.10], [A14.11], [A14.12]		273 – 523	0.01 – 5
Methanol	[A14.13]		313	0.002 – 0.04
***n*-Propanol**	[A14.14]		313	0.002 – 0.007
***2*-Propanol**	[A14.14]		313	0.002 – 0.01

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APPENDIX A.15. BINARY SYSTEMS CONTAINING 2-HEXANOL

Table A.15: Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with 2-hexanol

Components	References	Data rejected	Temperature range [K]	Pressure range [MPa]
Nitrogen	[A15.1]		333 – 393	2 – 10
Water	[A15.2], [A15.3], [A15.4]		273 – 363	0.1

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APPENDIX A.16. BINARY SYSTEMS CONTAINING 2-HEPTANOL

Table A.16: Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with 2-heptanol

Components	References	Data rejected	Temperature range [K]	Pressure range [MPa]
Nitrogen	[A16.1]		333 – 393	2 – 10
Water	[A16.2], [A16.3]		273 – 363	0.1

REFERENCES

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APPENDIX A.17. BINARY SYSTEMS CONTAINING 2-OCTANOL

Table A.17: Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with 2-octanol

Components	References	Data rejected	Temperature range [K]	Pressure range [MPa]
Nitrogen	[A17.1]		333 – 393	2 – 10
Water	[A17.2], [A17.3], [A17.4]		273 – 363	0.1

REFERENCES

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APPENDIX A.18. BINARY SYSTEMS CONTAINING *3*-PENTANOL

Table A.18: Sources of vapour-liquid and liquid-liquid equilibria data for binary systems with 3-pentanol

Components	**References**	**Data rejected**	**Temperature range [K]**	**Pressure range [MPa]**
***n*-Heptane**	[A18.1], [A18.2]		313 – 368	0.003 – 0.1
Benzene	[A18.3]		313	0.003 – 0.02
Carbon dioxide	[A18.4]		313	2 – 8
Water	[A18.5], [A18.6], [A18.7], [A18.8], [A18.9]		273 – 490	0.1
Methanol	[A18.10]		313	0.003 – 0.04

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APPENDIX B. CALCULATION OF UNCERTAINTIES ON TEMPERATURE AND PRESSURE

Calculations of the uncertainties on pressure and temperature measurements are similar. They are two sources of uncertainty: the uncertainty linked to the repeatability of measurements and the uncertainty of calibration. It is expressed by Equations (B.1) and (B.2):

$$u(T, K = 2) = 2\sqrt{u_{rep}^2(T) + u_{calib}^2(T)} = \sqrt{u_{rep}^2(T) + u_{ref}^2(T) + u_{corr}^2(T)} \tag{B.1}$$

$$u(P, K = 2) = 2\sqrt{u_{rep}^2(P) + u_{calib}^2(P)} = \sqrt{u_{rep}^2(P) + u_{ref}^2(P) + u_{corr}^2(P)} \tag{B.2}$$

where *2* is the coverage factor to better represent the uncertainty on the measurement. With $K=2$, the confidence is about 95%.

U_{rep}, u_{ref} and u_{corr} are defined by the same kind of equations for both temperature and pressure. They are expressed below for a physical parameter θ.

B.1. UNCERTAINTY OF MEASUREMENTS REPEATABILITY

The uncertainty of measurements repeatability is defined as (Equation (B.3)):

$$u_{rep}(\theta) = \sqrt{\frac{1}{N(N-1)}\sum_{k=1}^{N}(\theta_k - \bar{\theta})^2} \tag{B.3}$$

where $\bar{\theta}$ is the average.

B.2. STANDARD UNCERTAINTY

The uncertainty on calibration u_{ref} is a standard uncertainty of type B. The probability of distribution of the physical parameter θ considered follows a rectangular law. The probability of distribution is therefore unvarying in the interval $[3.\theta^-;\ \theta^+]$. $2a$ is the interval width. U_{ref} is defined by Equation (B.4).

$$u_{ref}(\theta) = \frac{a}{\sqrt{3}}$$

(B.4)

For the dead weight balance, a is equal to 200 mbar and 0.013 °C for the standard platinium probe 25 Ω.

B.3. UNCERTAINTY OF CALIBRATION

The calibration compares the values read and the one given by either the dead weight balance for pressure or the standard platinium probe for temperature. Thus, this correlation corrects the value of the parameter read on the probe. Second order equations have been considered for probes calibration (Equation (B.5)):

$$\theta = a_2\theta_{read}^2 + a_1\theta_{read} + a_0$$

(B.5)

The uncertainty of calibration is defined by Equation (B.6):

$$u_{corr}(\theta) = \sqrt{u^2(a_0) + \theta_{read}^2 u^2(a_1) + \theta_{read}^4 u^2(a_2) + 2\begin{bmatrix}\theta_{read}u(a_0,a_1) + \theta_{read}^2 u(a_0,a_2)\\ +\theta_{read}^3 u(a_{10},a_2)\end{bmatrix}}$$

(B.6)

B.4. UNCERTAINTIES OF TEMPERATURE AND PRESSURE MEASUREMENTS

Tables B.1 and B.2 present the uncertainties of respectively temperature and pressure measured for probes calibration.

Table B.1: Uncertainties of temperature measurements

Temperatures [°C]	**u (T_{bottom}, K=2) [°C]**	**u (T_{upper}, K=2) [°C]**
-20.007	0.018	0.019
-15.044	0.017	0.018
-10.040	0.017	0.017
-5.058	0.016	0.016

Table B.1 (to be continued): Uncertainties of temperature measurements

Temperatures [°C]	**u (T_{bottom}, K=2) [°C]**	**u (T_{upper}, K=2) [°C]**
-0.076	0.016	0.016
4.907	0.016	0.016
9.888	0.016	0.016
14.888	0.016	0.017
19.881	0.021	0.022
24.869	0.018	0.020
29.882	0.019	0.022
34.852	0.021	0.025
39.849	0.024	0.029

Table B.2: Uncertainties of pressure measurements

Pressures [bar]	**u (P) [bar]**
1.029	0.231
2.004	0.231
6.991	0.231
11.995	0.231
16.997	0.231
21.995	0.231
27.001	0.231
31.997	0.231
37.003	0.231
41.999	0.232

Table B.2 (to be continued): Uncertainties of pressure measurements

Pressures [bar]	u (P) [bar]
52.002	0.232
57.004	0.232
62.001	0.232
67.001	0.233
72.000	0.233
76.999	0.234
81.996	0.234

APPENDIX C. EXPERIMENTAL COMPOSITION OF THE LIQUID AND THE VAPOUR PHASES FOR MIX 2

Table C.1: Experimental composition of the liquid phase for MIX 2. u: uncertainty of measurements results from calibration.

Temperatures [K]	**Pressures [MPa]**	**Carbon dioxide**	**Hydrogen sulphide**	**Methane**	**Ethane**	**Propane**	**Cyclopentane**	**Benzene**	**Toluene**	***m*-Xylene**
283.18	1.49	0.0865	0.529	0.00243	0.00318	0.00081	0.00866	0.227	0.118	0.0250
313.19	3.49	0.1463	0.565	0.00793	0.00517	0.00089	0.00897	0.138	0.106	0.0216
338.19	5.39	0.1634	0.548	0.01148	0.00563	0.00089	0.00860	0.137	0.104	0.0211

u (z Carbon dioxide)	**u (z Hydrogen sulphide)**	**u (z Methane)**	**u (z Ethane)**	**u (z Propane)**	**u (z Cyclopentane)**	**u (z Benzene)**	**u (z Toluene)**	**u (z *m*-Xylene)**
2E-03	9E-03	7E-05	1E-04	2E-05	3E-04	6E-03	3E-03	8E-04
3E-03	9E-03	2E-04	2E-04	3E-05	3E-04	4E-03	3E-03	7E-04
3E-03	9E-03	3E-04	2E-04	2E-05	3E-04	4E-03	3E-03	6E-04

Table C.2: Experimental composition of the vapour phase for MIX 2. u: uncertainty of measurements results.

Temperatures [K]	**Pressures [MPa]**	**Carbon dioxide**	**Hydrogen sulphide**	**Methane**	**Ethane**	**Propane**	**Cyclopentane**	**Benzene**	**Toluene**	***m*-Xylene**
283.17	1.50	0.429	0.500	0.0576	0.00556	0.00086	0.0005	0.005	0.0019	0.0004
313.23	3.50	0.433	0.468	0.0740	0.00548	0.00083	0.0009	0.011	0.0050	0.0010
336.82	5.42	0.408	0.493	0.0663	0.00502	0.00080	0.0012	0.017	0.0068	0.0013

u (z Carbon dioxide)	**u (z Hydrogen sulphide)**	**u (z Methane)**	**u (z Ethane)**	**u (z Propane)**	**u (z Cyclopentane)**	**u (z Benzene)**	**u (z Toluene)**	**u (z *m*-Xylene)**
8E-03	9E-03	2E-05	2E-04	2E-05	2E-05	1E-04	6E-05	1E-05
7E-03	9E-03	2E-04	2E-04	2E-05	3E-05	4E-04	1E-04	3E-05
7E-03	9E-03	2E-04	1E-04	2E-05	4E-05	5E-04	2E-04	4E-05

APPENDIX D. EXPERIMENTAL HYDRATE DISSOCIATION CONDITIONS OF MIX 3 AND 4

Table D.1: Experimental hydrate dissociation conditions in the presence of distilled water of MIX 3 (Table 2.5)

Aqueous Fractions	**Temperatures [K] (±0.03)**	**Pressures [MPa] (±0.001)**
0.758	290.85	3.434
0.872	290.65	3.904
0.891	290.85	4.565

Uncertainties are calculated and presented for these experimental results in Appendices E and F.

Table D.2: Experimental hydrate dissociation conditions in the presence of distilled water of MIX 4 (Table 2.6)

Aqueous Fractions	**Temperatures [K] (±0.03)**	**Pressures [MPa] (±0.001)**
0.716	295.68	4.277
0.758	295.79	5.734
0.765	296.14	8.063

APPENDIX E. CALCULATION OF UNCERTAINTIES ON HYDRATE DISSOCIATION POINT MEASUREMENTS

As seen on Figure 2.7, the hydrate dissociation point is determined as the intersection between two curves. Depending on the tendency curve used to represent the different point, there is an uncertainty, more or less important, on the pressure and the temperature calculated. In addition to this uncertainty, the uncertainty on calibration of temperature and pressure probes is also considered.

E.1. UNCERTAINTY ON CALIBRATION

The uncertainty on calibration u_{calib} is a standard uncertainty of type B. The probability of distribution of the physical parameter θ considered follows a rectangular law. The probability of distribution is therefore unvarying in the interval $[3.\theta^{-}; \theta^{+}]$. $2a$ is the interval width. The uncertainty u_{calib} is calculated by Equation (E.1):

$$u_{calib}(\theta) = \frac{a}{\sqrt{3}} \tag{E.1}$$

E.2. UNCERTAINTY ON HYDRATE DISSOCIATION POINT MEASUREMENT

The uncertainty on hydrate dissociation point measurement has two sources of uncertainties: the uncertainty on temperature and the one on pressure.

The physical parameter θ can be expressed as a function of independent parameters α_k (Equation (E.2)):

$$\theta = f(\alpha_1, \alpha_2, \dots, \alpha_N) \tag{E.2}$$

The uncertainty on the hydrate dissociation point measurement u can be expressed as (Equation (E.3)):

$$u(\theta, K = 2) = 2\sqrt{\sqrt{\sum_{k=1}^{N} \left(\frac{\partial f}{\partial \alpha_k}\right)^2} u^2(\alpha_k) + u_{calib}^2(\theta)} \tag{E.3}$$

where *2* is the coverage factor to better represent the uncertainty on the measurement. With *K=2*, the confidence is about 95%.

In the case of hydrate point measurement, the uncertainty is about the temperature and the pressure of the intersection of two slopes.

The curve before the dissociation point is usually a second-order polynomial equation (Equation (E.4)):

$$P = A^{"}T^2 + B^{"}T + C^{"} \tag{E.4}$$

And the curve after the dissociation point is usually a straight line (Equation (E.5)):

$$P = A'T + B' \tag{E.5}$$

The temperature of hydrate dissociation is defined as (Equation (E.6)):

$$A^{"}T^2 + B^{"}T + C^{"} = A'T + B' \tag{E.6}$$

It is equivalent to solve the following equation (Equation (E.7)):

$$A^{"}T^2 + \left(B^{"} - A'\right)T + \left(C^{"} - B'\right) = 0 \tag{E.7}$$

The temperature of hydrate dissociation point *T** is thus defined by Equation (E.8).

$$T^* = \frac{-\left(B^{"} - A'\right) + \sqrt{\Delta}}{2A^{"}}$$

with

$$\Delta = \left(B^{"} - A'\right)^2 - 4A^{"}\left(C^{"} - B'\right) \tag{E.8}$$

and

$$P^* = A^{"}T^{*2} + B^{"}T^* + C^{"}$$

Thus the temperature depends on parameters *A"*, *B"*, *C"*, *A'* and *B'*. The uncertainty on the temperature can be defined as follows (Equation (E.9)):

$$u(T^*, K=2) = 2\sqrt{\left[\frac{\partial T^*}{\partial A''}u_c(A'')\right]^2 + \left[\frac{\partial T^*}{\partial B''}u_c(B'')\right]^2 + \left[\frac{\partial T^*}{\partial C''}u_c(C'')\right]^2 + \left[\frac{\partial T^*}{\partial A'}u_c(A')\right]^2 + \left[\frac{\partial T^*}{\partial B'}u_c(B')\right]^2 + u_{calib}^2(T)} \tag{E.9}$$

where $u_c(\alpha_k)$ is the variance of the parameter α_k, defined after a linear regression of parameters.

As for the pressure, it can be calculated by Equation (E.5). Thus it is dependent on parameters *A'* and *B'* and the temperature *T** (Equation (E.10)).

$$u(P^*, K=2) = 2\sqrt{\left[\frac{\partial P^*}{\partial A''}u_c(A'')\right]^2 + \left[\frac{\partial P^*}{\partial B''}u_c(B'')\right]^2 + \left[\frac{\partial P^*}{\partial C''}u_c(C'')\right]^2 + \left[\frac{\partial P^*}{\partial T^*}u(T^*)\right]^2 + u_{calib}^2(P)} \tag{E.10}$$

In the case if the curve before the dissociation point is a straight line, Equation (E.4) becomes Equation (E.11):

$$P^* = B''T + C'' \tag{E.11}$$

Then the temperature of dissociation point is defined as (Equation (E.12)):

$$T^* = \frac{B' - C''}{B'' - A'} \tag{E.12}$$

The uncertainty on temperature is expressed by Equation (E.13):

$$u(T^*) = 2\sqrt{\left[\frac{\partial T^*}{\partial B''}u_c(B'')\right]^2 + \left[\frac{\partial T^*}{\partial C''}u_c(C'')\right]^2 + \left[\frac{\partial T^*}{\partial A'}u_c(A')\right]^2 + \left[\frac{\partial T^*}{\partial B'}u_c(B')\right]^2 + u_{calib}^2(T)} \tag{E.13}$$

And Equation (E.10) becomes Equation (E.14):

$$u(P^*, K=2) = 2\sqrt{\left[\frac{\partial P^*}{\partial A'}u_c(A')\right]^2 + \left[\frac{\partial P^*}{\partial B'}u_c(B')\right]^2 + \left[\frac{\partial P^*}{\partial T^*}u(T^*)\right]^2 + u_{calib}^2(P)} \tag{E.14}$$

An example is given in Table E.1 for hydrate dissociation conditions of MIX 3 (Table D.1).

Table E.1: Experimental hydrate dissociation conditions in the presence of distilled water of MIX 3 and corresponding uncertainties

Temperatures [K]	u(T, K=2) [K]	Pressures [MPa]	u(P, K=2) [MPa]
290.9	3.7	3.4	0.2
290.7	2.4	3.9	0.4
290.9	0.07	4.6	0.1

N.B.: *Since bubble point measurement follows the same procedure as for hydrate dissociation point measurement, uncertainties can be calculated in the same way.*

APPENDIX F. CALCULATION OF UNCERTAINTIES ON AQUEOUS MOLE FRACTION

For a binary system, the aqueous mole fraction is defined as (Equation (F.1)):

$$x_{aq} = \frac{n_{aq}}{n_{aq} + n_2} \tag{F.1}$$

The uncertainty is given by Equation (F.2)

$$u(x_{aq}) = \sqrt{u_{rep}^2(x_{aq}) + \left(\frac{\partial x_{aq}}{\partial n_{aq}}\right)_{n_2}^2 u^2(n_{aq}) + \left(\frac{\partial x_{aq}}{\partial n_2}\right)_{n_{aq}}^2 u^2(n_2)}$$

whether

$$u(x_{aq}) = \sqrt{u_{rep}^2(x_{aq}) + \left(\frac{1 - x_{aq}}{n_{aq} + n_2}\right)^2 u^2(n_{aq}) + \left(\frac{x_{aq}}{n_{aq} + n_2}\right)^2 u^2(n_2)} \tag{F.2}$$

In our case, measurements are not always repeated, so u_{rep} cannot be calculated. But if they are repeated, it can be calculated as shown in Appendix B.

The number of moles n_i is determined with the volume injected. The mixture prepared is always loaded as a single mixture, under liquid phase. The aqueous solution is also under liquid state. In both cases, it is assumed that the operating temperature is not influencing the density of the fluids. Then the uncertainty on n_i can be calculated with the following simplified equation (Equation (F.3)):

$$u(n_i) = \frac{\rho_i}{M_i} u(V_i) \tag{F.3}$$

In the following part, uncertainties are given for calculated aqueous mole fractions for the experimental work presented in Table D.1 (MIX 3). The uncertainties on volumes are given by the manufacturers. The uncertainty on the pump is $0.3\%_{vol}$ and on the external cylinder 2.10^{-2} cm^3. Thus the calculated uncertainties are given in Table F.1.

Table F.1: Experimental aqueous fraction and corresponding uncertainties of hydrate dissociation conditions of MIX 3 (Table 2.5)

Aqueous Fractions (x_{aq})	**u(x_{aq}, K=2)**
0.758	0.009
0.872	0.004
0.891	0.008

APPENDIX G. LIST OF PUBLICATIONS

G.1. ARTICLE

Hajiw, M., Chapoy, A., Coquelet, C., *Hydrocarbons - Water Phase Equilibria using the CPA Equation of State with a Group Contribution Method*, The Canadian Journal of Chemical Engineering, 2014, DOI: 10.1002/cjce.22093

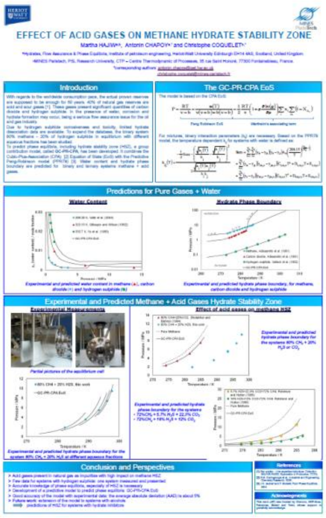
G.2. CONFERENCES

- **SFGP 2013** (oral presentation):

Hajiw, M., Chapoy, A., Coquelet, C., *Hydrocarbons - Water Phase Equilibria using the CPA Equation of State with a Group Contribution Method*

- **ICGH 8** (poster)

Hajiw, M., Chapoy, A., Coquelet, C., *Effect of Acid Gases on Methane Hydrate Stability Zone*



EFFECT OF ACID GASES ON METHANE HYDRATE STABILITY ZONE

Martha HAJIW, Antonin CHAPOY and Christophe COQUELET

Introduction

The GC-PR-CPA EoS

Predictions for Pure Gases + Water

Water Content

Hydrate Phase Boundary

Experimental and Predicted Methane + Acid Gases Hydrate Stability Zone

Experimental Measurements

Effect of acid gases on methane HSZ

Conclusion and Perspectives

References

Acknowledgments

- **AIChE 2014** (poster):

Hajiw, M., Chapoy, A., Coquelet, C., *Methanol Content in Natural Gas Systems: Modelling with the GC-PR-CPA Eos*

G.3. INDUSTRIAL PROJECTS

- **Joint Industrial Project "Gas Hydrates and Flow Assurance":**

The aim of this project is to deal with gas hydrate problems in subsea pipelines. It is mainly focused on sour and acid gases, at different concentrations. Different studies are conducted, including the impact of thermodynamic inhibitors on hydrate stability zone, inhibitor distribution in water, hydrate formation in low water content. The development of the thermodynamic model is part of this project and has been developed in six Progress Reports (01 to 05), as well as experimental measurements.

- **Joint Industrial Project "Impact of Common Impurities on CO_2 Capture, Transport and Storage":**

In the context of Carbon Capture, Transport and Storage (CCS), the impact of impurities on carbon dioxide transported is studied. The presence of these impurities during transport may lead to flow assurance issues, such as gas hydrate formation. The aim of this project is to study the phase behaviour of carbon dioxide in the presence of impurities and their properties (viscosity and density). Experimental measurements have been presented in two Progress Reports (01 and 02).

- **Gas Processors Association "Impact of Aromatic on Acid Gas Injection":**

When the natural gas is produced, acid gases are usually removed with different types of amines before being compressed for injection in underground formations. However, amines can also absorb aromatic compounds. The aim of this project is to investigate the impact of aromatics on acid gas compression design. Indeed they can condense at high pressures and lead to liquid formation in compressors or hydrate formation. Experimental measurements have been included in one Progress Report (March 2014).