Phase equilibrium and liquid mole fraction measurements of tetra-n-butylammonium chloride + CO₂ and CH₄ semi-clathrates

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Education is the passport to the future, for tomorrow belongs to those who prepare for it today – Malcolm Little

Abstract

Gas hydrates have many potential industrial applications in gas storage and transportation, particularly for the purpose of reducing energy consumption thus carbon footprint in the transportation of natural gas. Regarding gas storage, the possibility of reducing greenhouse gas emissions via the sequestration of carbon dioxide in the form of gas hydrates. However, to scale up these technologies a fundamental understanding of their formation is required. They require high pressures and low temperatures to form. One of the low-cost alternatives consists of using thermodynamic promoters such as tetra-n-butylammonium chloride (TBAC). These promoters reduce the hydrate equilibrium conditions making them more energetically favorable, allowing higher temperatures and lower pressures to form hydrates. This thesis investigates and studies the three-phase equilibrium conditions and liquid mole fraction measurements of CH₄-TBAC-H₂O and CO₂-TBAC-H₂O semi-clathrates. The importance of these liquid mole fraction measurements is for use in reactor design and kinetic models. Concentrations of 5-wt%, 10-wt% and 15-wt % of TBAC were employed. Results from this study show that the thermodynamic promoter used has a significant effect in reducing the semi-clathrate equilibrium conditions for both methane and carbon dioxide. For methane, a pressure range of 0.8 MPa to 4.7 MPa, a temperature range of 280 to 290 K were used with a corresponding mole fraction range from 0.37x10⁻³ to 1.88x10⁻³. For carbon dioxide, the pressure range was from 0.1 to 2.4 MPa and temperature was varied from 277 to 288 K with a corresponding mole fraction from 1.42×10^{-3} to 18.75×10^{-3} .

Résumé

Les hydrates de gaz ont de nombreuses applications industrielles potentielles dans l'entreposage et le transport du gaz, en particulier dans le but de réduire la consommation d'énergie de l'empreinte carbone ainsi dans le domaine du transport de gaz naturel. En termes de stockage de gaz, la possibilité de réduire les émissions de gaz à effet de serre par la séquestration du dioxyde de carbone sous la forme d'hydrates de gaz. Cependant, pour le passage à grande échelle de ces technologies une compréhension fondamentale de leur formation n'est requise. Ils exigent généralement une haute pression et très basse température à la forme. L'une des alternatives à faible coût consiste en l'utilisation de promoteurs thermodynamique comme tetra-nbutylammonium (TBAC). Ces promoteurs de réduire les conditions d'équilibre de l'hydrate de les rendre plus favorable énergétiquement, permettant à des températures et pressions plus basses pour former des hydrates de gaz. Cette thèse étudie et étudier les conditions d'équilibre en trois phases liquides et des mesures de la fraction molaire de CH4-TBAC-H2O et CO2-TBAC-H2O semiclathrates. L'importance de ces mesures de fraction molaire liquide est à utiliser dans la conception du réacteur et des modèles cinétiques. Les concentrations de 5-wt %, 10-wt % et 15-wt % du TBAC ont été employées. Les résultats de cette étude montrent que le promoteur thermodynamique utilisé a un effet significatif dans la réduction de la demi-les conditions d'équilibre pour les clathrates de méthane et dioxyde de carbone. Pour le méthane, une plage de pression de 0,8 MPa à 4,7 MPa, la gamme de température de 280 à 290 K ont été utilisés avec une fraction molaire correspondante vont de $0,37 \times 10^{-3}$ à $1,88 \times 10^{-3}$. Pour le dioxyde de carbone, l'intervalle de pression a été de 0,1 à 2,4 MPa et la température variait de 277 à 288 K avec une fraction molaire correspondante de $1,42 \times 10^{-3}$ à 18.75×10^{-3} .

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List of abbreviations

Nomenclature

Α	Component-specific constant Antoine equation
В	Component-specific constant Antoine equation
С	Component-specific constant Antoine equation
d(lnk)/d(1/T)	Temperature dependence constant (K)
kg	Guest gas Henry's constant
kgo	Henry's law constant for solubility in water at 298.5 K
Mi	molar mass of component i (g/mol)
m _b	mass of sample taken in the bomb (g)
Р	Pressure (Pa)
R	Universal gas constant
Т	Temperature (K)
TBAC	Tetra-n-butylammonium chloride
u	uncertainty
V	Volume
Х	Mole Fraction
Y	variable
n	number of moles

Subscripts

g	gas
TBAC	Tetra-n-butylammonium chloride
Т	Total
W	water

Superscripts

amb	ambient
L	liquid
V	vapor

1. Introduction

In our days, the planet's number one enemy is called global warming. It is real, and it came to stay if we do not act to fight it. The new generations face enormous challenges of the size of the world which are to find new energetic alternatives more favorable for the environment, reduction of the emissions of greenhouse gases, reduction of the carbon footprint in all the processes and economic activities of the human being. The path will not be easy and will require the commitment, action, and implementation of all machinery and infrastructure available at all levels, the initiative must start from any citizen to companies and especially governments that make the big decisions that impact and guide the course of future generations. Ideas and solutions are many, they have been exposed and are on the table to be implemented on a large scale. Climate change is global on its causes and consequences and the response requires international collective action. Working together is essential to respond to the scale of the challenge [1].

One of the solutions that focuses on the field of energy, natural gas transportation, and storage of gases of environmental interest, is the use of gas hydrates. These compounds promise to be an alternative to capture and store carbon dioxide and thus reduce the impact of this gas on the environment, as well as a good resource to transport natural gas at a lower energy cost. It also promises to be a good solution for storing hydrogen, which would solve the storage problem, the main limitation of this technology with great ecological potential. Finally, gas hydrates can act as means for separating industrial flue gases [2]. The understanding of gas hydrate formation and growth is crucial for its application on an industrial scale, which is the objective of this work.

The core of this research was the phase equilibrium and the liquid mole fraction measurements in two systems: methane-Tetrabutylammonium Chloride (TBAC)-H₂O and carbon dioxide-TBAC-H₂O. The scope of my work were to determine the solubility of the guest gases at different TBAC concentrations, temperatures and pressures. For both experiments, a graph of phase equilibrium of pressure vs temperature, molar fraction vs temperature and pressure vs molar fraction is reported.

2. Background

2.1 Global warming

The first documented prediction about climate change due to human activities was made by the Swedish chemist Svante Arrhenius in 1896 [3][4]. Today more than 100 years later, that prediction has become true, and the problem has become acute in recent years. Arrhenius realized that the amount of carbon dioxide being released into the atmosphere was increasing because of the industrial revolution. He estimated carbon dioxide concentration would continue to increase as the world's consumption of fossil fuels, especially coal. The exceptional understanding of Arrhenius regarding carbon dioxide related to global warming led him to predict that if atmospheric carbon dioxide doubled, Earth would become several degrees warmer [3][5]. After an estimated 10,000 to 100,000 calculations by hand [6], Arrhenius predicted a temperature rise of 5 °C to 6 °C, nearly from recent estimates of 1.5 °C to 4.5 °C [7]. The rates of warming in the coming years are expected to be up to 100 times faster than any experienced in the past [8]. The increase in temperature will be more in middle and higher latitudes like in Canada, mostly in winter, than in the tropics. The scientists also predict that if no actions are taken to limit greenhouse gas emissions, by around 2030 carbon dioxide concentrations in the atmosphere will be twice those in pre-industrial times [9]. In 2005, the concentration of carbon dioxide (Figure 1) exceeded by far the natural range over 650,000 years (180-300 ppm) as determined from ice cores [10]. Similarly, the atmospheric concentration of methane (Figure 1) has increased from 715 ppb before the industrial revolution to 1732 ppb in the 1990s, and up to 1,774 ppb in 2005. The atmospheric concentration of methane in 2005 exceeded by far the natural range of the last 650,000 years (320 to 790 ppb) as determined as well from ice cores. The increase of methane concentration is due to human activities, substantially agriculture and fossil fuel use [10]. This increase of methane is much higher than the rise seen over the last half-million years of glacial-interglacial cycles.

Humankind is now aware that carbon dioxide in the atmosphere is increasing, it would double by the middle of this century from the levels at the time of Arrhenius [5]. However, some environmental policies of governments dismiss and overlook the imminent threat of global warming. The carbon emissions from fossil fuels per person in the United States are ten times greater than in third world countries [11]. In 1958, Charles David Keeling was the first person to measure the concentration of atmospheric carbon dioxide with high accuracy. His work is a significant contribution to track the concentration of this greenhouse gas because the measurements maintain the accuracy and precision to separate fossil fuels emissions from those due to the natural annual cycle of the biosphere. Keeling's research constitutes the master time series documenting the changing composition of the atmosphere [12][13]. Observations of parallel trends in the atmospheric abundances of the ${}^{13}CO_2$ isotope [14] and O_2 [15]distinctively identify this increase in carbon dioxide coming from fossil fuel burnings [10].



Figure 1. The concentrations and radiative forcing by (a) carbon dioxide (CO₂), (b) methane (CH₄) and (c) nitrous oxide (N₂O) over the last 20,000 years reconstructed from Antarctic and Greenland ice and firm data (symbols) and direct atmospheric measurements (panels a, b, c, red lines). The grey bars show the reconstructed ranges of natural variability for the past 650,000 years. The width of the age spread in the ice data varies from about 20 years for sites with a high accumulation of snow such as Law Dome, Antarctica, to about 200 years for low-accumulation sites such as Dome C, Antarctica. The arrow shows the peak in the rate of change in radiative forcing that would result if the anthropogenic signals of CO₂, CH₄, and N₂O had been smoothed corresponding to conditions at the low-accumulation Dome C site [10].

The most predominant gases in the atmosphere, nitrogen and hydrogen, are transparent to the radiation incoming from the Sun and the radiation outgoing from the Earth thus their warming effect is little or null. The gases that are not transparent are water vapor, ozone, carbon dioxide, methane, nitrous oxide (Figure 1), and chlorofluorocarbons are also known as greenhouse gases [5]. These last three gases classified as trace gases could rival or even exceed that of the increasing concentration of carbon dioxide [16][17]. Trace gases are present at concentrations that are two to six orders of magnitude lower than carbon dioxide but are significant because they absorb more radiation than carbon dioxide. Methane has per mole a global warming potential 3.7 times that of

carbon dioxide [18]. According to Hansen et al. [19] traces are responsible for 43% of the increase in radioactive forcing.

Another potential threat to climate change could literally emerge from the sea. This hazard seems to accentuate warming tendencies. This hazard is the possible release of methane from the permafrost or from under the oceans as the temperatures rise [20].



CHANGES IN TEMPERATURE, SEA LEVEL AND NORTHERN HEMISPHERE SNOW COVER

Figure 2. Observed changes in (a) global average surface temperature, (b) global average sea level from tide gauge (blue) and satellite (red) data and (c) Northern Hemisphere snow cover for March-April. All changes are about corresponding averages for the period 1961–1990. Smoothed curves represent decadal average values while circles show yearly values. The shaded areas are the uncertainty intervals estimated from a comprehensive analysis of known uncertainties (a and b) and from the time series (c) [10].

The countless consequences of global warming caused by the temperatures rise (Figure 2) at the current pace would be catastrophic. For example, declining of rainfall at middle latitudes could

affect the food chain production, sea level rise (Figure 2) between 0.3 and 1.1 meters by 2100 [21] could displace millions of people from their place of origin specifically in developing countries [22]. The following millennia after the ice age ended approximately 21,000 years ago, the global sea level rose by about 120 m and stabilized between 3,000 and 2,000 years ago. Sea level did not change significantly from then until the late 19th century (Figure 2). The record of modern sea level change shows evidence for the beginning of sea level rise during the 19th century. Estimates for the 20th century show that global average sea level increased at a rate of about 1.7 mm year⁻¹ [10]. Global warming could cause changes in species distribution and abundance and have serious implications for human health. The increase in mosquito-borne diseases has been reported in the highlands of Asia, Central Africa and Latin America [23]. Plasmodium falciparum that causes malaria has been reported for the first time up to 2100 m in the highlands of Papua New Guinea, Tanzania, and Kenia. Moreover, dengue fever, formerly restricted to live below 1000 m in elevation and 10 °C in winter, has appeared at 1700 m in Mexico. Aedes aegypti, a vector of dengue and yellow fever viruses, has recently been reported at 2200 m in Colombia [23]. The increase in atmospheric carbon dioxide can affect biogeochemical cycles of carbon, oxygen, and nutrients that cause changes in the ocean. The rise in atmospheric carbon dioxide causes additional CO₂ to dissolve in the ocean. Changes in temperature and salinity affect the solubility and equilibrium of gases. The biogeochemical changes also affect biological activity, with additional consequences for marine life [10].

For all the consequences above of global warming, new solutions must be developed to tackle this problem to ensure that the life of all species including humans is preserved. A promising solution for global warming is gas sequestration and storage. This technology can contribute significantly to reduce the concentration of carbon dioxide and methane present in the atmosphere and store them in a feasible form. Furthermore, the carbon footprint can be reduced by using less energy demanding technologies to storage and transport natural gas.

2.2 Clathrate hydrates

Formed in nature 1800 million years ago [2] and discovered in the laboratory in 1810 by Sir Humphry [24], clathrates hydrates or gas hydrates (GH) are non-stoichiometric and crystalline structures formed by combining water and low molecular weight guest gases. The guest compounds of these structures are gases or volatile at atmospheric conditions and thus are also referred to as gas hydrates [25]. These gases are entrapped inside a water molecule lattice linked through hydrogen bonding, under suitable conditions of low temperature and elevated pressure [2][26]. Gas hydrates can be found in nature below the permafrost and in subsea sediments where suitable conditions are present. Figure 3 shows the locations of gas hydrates on Earth.



Figure 3. Location of gas hydrates [120].

It is estimated that more than half of carbon resources available on Earth are stored in hydrate form. This amount exceeds all other reserves as fossil fuels, soil, and living organisms [27].

Over the following 125 years, researchers in the field had two major goals, namely to identify all the compounds that formed hydrates and to quantitatively describe the compounds by their compositions and physical properties [2].

Since the discovery of hydrates, various applications have been proposed taking advantage of hydrate properties. The oil and gas industry was one of the first interested in studying its behavior since the formation of hydrates inside pipelines provokes blockages and plugs that caused significant economic losses. In 1934, Hammerschmidt published a paper mentioning the problem above. Research quickly began to focus on prevention of hydrates, also referred to as flow assurance, and continues to this day [28].

One relevant application is the use of hydrates to store carbon dioxide as a mean to mitigate global warming [29]. The concentration of this greenhouse gas in the atmosphere has significantly

increased over the past decades due to excessive use of fossil fuels. CO₂ capture and sequestration (CCS) have become an important field to tackle global warming as solution to this problem. The most expensive step in the CCS process is the CO₂ separation; the challenge is to develop technology capable of absorbing the CO_2 that is produced in large scale in the industry [30]. Another remarkable proposal is the possibility to remove the methane naturally present in the permafrost and ocean bed and replace it with CO₂ [31]. Hence, methane gas could be extracted, and the CO₂ could take its place and maintain the stability of the hydrate layer. Other applications include the replacement of the high energy demanding methods to store and transport fossil fuels such as liquefied natural gas (LNG) or compressed natural gas (CNG) by the hydrated form of natural gas [32]. Gas hydrates are currently considered a potential alternative energy resource because each volume of hydrate can contain as much as 184 volumes of gas at STP [2]. Sloan et al. [2] mention that hydrate reservoirs have been considered a substantial future energy resource because the amount of carbon stored is twice as great as the all the other fossil fuels combined; moreover, less than 15% of the recovered energy is required for dissociation. Hydrates found in nature typically have more than one guest gas [33]. Hence the fundamental knowledge of phase equilibrium is crucial to the successful implementation of this technology.

2.2.1 Clathrate structures

Three different types of hydrate structures are known until now, namely structure I (sI), II (sII) and H (sH) [2]. Structures I and II are found in nature, being sI the most common.

In sI, the cages are arranged in body-centered packing and are large enough to include methane, ethane, carbon dioxide, and hydrogen sulfide. These molecules must have molecular diameters in the range of 420-580 pm [34]. This structure is configured with two 5^{12} cavities, and six $5^{12}6^2$ cavities arrange themselves in a single unit cell. This cell consists of 46 water molecules and can be found in Figure 5. Common gas hydrate structures and the water cage types that compose the hydrate structures [2].

In sII, diamond packing is present resulting in some cages being large enough to include not only methane and ethane but also gas molecules as large as propane, isobutene, and nitrogen [35]. Structure II is formed when sixteen 5^{12} cavities and eight $5^{12}6^4$ cavities form a unit cell; it can be seen in Figure 5 [36].

In the late 1940s and early 1950s, von Stackelberg and coworkers summarized two decades of experiments in x-ray hydrates crystal diffraction. The interpretation of these results by von Stackelberg, Muller, Claussen, Pauling and Marsh led to the determination of two hydrate crystal structures (sI and sII) shown in Figure 4. Studies showed hydrates to be members of the class of compounds labeled "clathrates" by Powell in 1948 – after the Latin "clathratus" meaning "to encage" [2].

The existence of a third hydrate structure, structure H (sH) was not discovered until 1987. The unit cell of sH is shown in Figure 4. Structure H requires two inclusion molecules, a small molecule such as methane and carbon dioxide and larger molecules typical of a condensate or an oil fraction such as neohexane with a diameter in the range of 800-900 pm [2]. This structure requires three 5^{12} cavities, two $4^35^66^3$ cavities, and one $5^{12}6^8$ cavities to form one unit cell. This cell consists of 36 water molecules [36].



Figure 4. Hydrate crystal unit structures: (a) sI (McMullan and Jeffrey, 1965), (b) sII (Mak and McMullan, 1965) and (c) sH [2]

Figure 5 shows the different unit cells with the associated cavity types for the three different structures.



Figure 5. Common gas hydrate structures and the water cage types that compose the hydrate structures [2].

2.3 Applications of gas hydrates

Gas hydrate formation has numerous positive applications such as the use of clathrates hydrates as means of gas storage and transport, carbon dioxide sequestration, separation of different gases from flue gas streams, cool-storage, and hydrogen storage.

2.3.1 Carbon dioxide sequestration

The continuous increase in the concentration of carbon dioxide in the atmosphere due to human activities is estimated to cause significant changes in climate. Around 50% of the current carbon dioxide emissions are absorbed by the ocean and by land ecosystems [37][38]. The remaining amount wreaks havoes on the environment.

In a lecture in 1896 [39], Arrhenius estimated that doubled the concentration of carbon dioxide as a result of fossil fuel burning would take 3000 years. At that time he was in favor of the slow warming because he believed it could cause better living conditions and higher crop yields [4]. However, that Arrhenius's estimation and what he believed about slow warming got out of hand.

Carbon dioxide sequestration represents the largest available sink [40]. Some studies have been performed to evaluate the risks associated with carbon dioxide disposal in the ocean. This idea was first suggested in 1977 [41]. Carbon dioxide deposition in the ocean obtained by sequestration is being evaluated and is in the experimental stage to determinate the long-term stability and the impact on marine life [42]. Another suggestion is the use of depleted oil and gas reservoirs to store carbon dioxide in the hydrated form [43]. Environmental studies must be conducted to evaluate the viability of large scale operations.

2.3.2 Natural gas storage and transportation

The use of gas hydrates to supply natural gas systems was first suggested by Benesh in 1942 [44]. Methods such as compressed natural gas (CNG) or liquefied natural gas (LNG) require elevated pressure above 20 MPa, and low temperatures around -162 °C respectively [32] while gas hydrates can be transported at atmospheric pressure and milder temperatures above the ones required for LNG. However, gas density is lower in gas hydrates than CNG and LNG as shown in Table 1. Gas hydrates long-term storage is achieved at normal temperatures between 0 °C to -10 °C and pressures between 0.1 MPa to 1 MPa. Liquefied natural gas, compressed natural gas and gas hydrates can store 637, 200 and 167 m³ of gas respectively at standard operating temperature and pressure [32]. It is estimated that a cost reduction of 24% is achieved when natural gas is stored in hydrated form compared to LNG [45]. The development of a hydrate vessel loaded with pellets was built in Japan for the purpose of transporting natural gas [46] along with the beginning of a process plant to produce these hydrate pellets.

Small cages for methane	Energy density (Kcal/m ³)
sI	5.32×10^5
sII	1.46 x 10 ⁶
sH	1.90 x 10 ⁶
LNG at -160 °C	6.00 x 10 ⁶

Table 1. Energy density of all three hydrate structures and the liquefied natural gas [45].

2.3.3 Pipeline blockage

Gas hydrates formation hinders pipelines in the oil and gas industry causing an economic loss due to stop flow. The blockage of pipelines by hydrates can result in production stoppage for up to several months while the hydrates dissociate [36]. These cloggings were first discovered in the 1930's, the presence of high pressures, low temperatures, water, methane and other small hydrocarbons allow gas hydrates to form and plug pipelines [47] as can be seen in Figure 6.



Figure 6. A large gas hydrate plug formed in a subsea hydrocarbon pipeline. Picture from Petrobras (Brazil) [121]

Due to pipeline blockages, researchers have been focused on studying this problem since the 1930's. One of the challenges of dealing with this problem in the field is the accumulation of local pressure when the formation of plugs. This process has the potential risk of creating high-velocity projectiles as plugs decompose. Figure 7 illustrates the hydrate formation in pipelines.



Figure 7. Conceptual picture of hydrate formation in a multiphase flow line used in the CSM Hydrate Kinetic model, CSMHyK [122].

Moreover, if the cluster is heated, it is likely to detach from the wall. If the pipeline is highly pressurized, the result could be a projectile shooting through the pipeline. According to some measurements, the speed of that projectile has been 300 km/h [36]. At this velocity, it is highly probable the pipeline to be damaged.

The use of inhibitors has been proposed to prevent gas hydrates formation. Research in this field has been undertaken focused on studying and designing chemical additives to perform and improve thermodynamic, kinetic and anti-agglomeration conditions [48]. Thermodynamic inhibitors change the hydrate form conditions. These inhibitors such as glycol and methanol are widely used, but in large quantities of up to 60% [49] also, alcohols are difficult to regenerate and reuse [2]. For these reasons, the development of more efficient additives is crucial to achieving efficiency and environmental goals. Kinetic and anti-agglomeration inhibitors retard hydrate formation time and growth rate while increasing the residence time the gas remains in the pipeline. These inhibitors operate between 0.1 and 1% [49].

2.3.4 Separation processes

Gas hydrates have the potential to be used as a means of separating flue gas stream since they contain water and the hydrate-forming substances solely with a composition in the hydrate crystal different that in the original mixture.

The most expensive step of the capture of carbon dioxide and sequestration (CCS) is the CO₂ separation. The challenge is to develop energy efficient and environmentally friendly technologies to capture CO₂ [50]. One innovative proposal is the use of gas hydrates to separate carbon dioxide from combustion flue gas. As a result of the difference in affinity between carbon dioxide and other gases in the hydrate cages when the formation of hydrate crystals is taking place from a mixture of gases, the concentration of CO₂ in the hydrate phase increases at the same time the concentration of other gases increases in the gas phase. Afterward, the hydrate phase can be deformed by depressurization, and therefore CO₂ can be recovered [51][50]. Carbon dioxide selectivity in the hydrate phase can be at least four times higher than in the gas phase [52].

Furthermore, gas hydrates have been proposed to be used as an alternative to concentrate temperature sensitive and viscous solutions [53] or to recover encapsulated proteins from reversed micellar solutions in concentrated form [54]. In the 1960s and 1970s, some studies were performed to evaluate the possibility of water desalination by using gas hydrates. Even though the process was feasible technically speaking, it was not economically sustainable to put it into practice industrially [25]. Separation of methane from emitted industrial gas streams has attracted significant attention in the last few decades since this gas is the largest constituent of natural gas streams. Natural gas reserves in the form of hydrates in the Earth have a greenhouse effect 21 times greater than that of CO_2 and contribute to the global greenhouse effects [55][56].

2.3.5 Cool-storage

The consumption of energy for air-conditioning has increased year by year. Therefore, some energy-saving solutions have been proposed to tackle greenhouse gas emissions and thus reduce the carbon footprint. One of this solutions is the use of regenerative air-conditioning systems. Clathrate hydrate slurry (CHS) is a cooling medium for use in air-conditioning systems which enables storage and transportation of cooling at a high thermal density. Due to the phase change involved in the gas hydrate formation from an aqueous solution, clathrate hydrate slurries are projected as a potential refrigerant. The phase above change temperature above the freezing point of water and the large heat of fusion [57] make CHS a prominent alternative in the field of air conditioning [2]. Hidemasa and Shingo at JFE Steel Corporation® in Japan proposed and developed CHS to be used in next-generation energy-saving air-conditioning systems. CHS is appropriate for cooling applications since it has a latent heat in the range of 5-12 °C, has a cooling storage capacity up to 3 times greater than the conventional chilled water. CHS is a cooling medium with a high thermal density that can reduce the energy consumption, reduce CO₂ emissions and decrease cooling medium transportation in the air-conditioning systems [58]. CHS air-conditioning systems could potentially be charged at night taking advantages of the off-peak electricity and discharged during the day [59]. Several more studies are being conducted to evaluate the features of the CHS as refrigerants [60].

2.3.6 Hydrogen storage

Hydrogen is one of the most prominent environmental friendly sources of energy. Hydrogen has emerged as the fuel of the future for its abundance in the universe, it cannot be destroyed unlike hydrocarbons, and it simply changes state from water to hydrogen and back to water during consumption. The pollutants such as CO, CO₂, NO_X, SO_X emitted by fossil fuels are harmful to the environment unlike those produced by hydrogen [61]. The safe storage of hydrogen is crucial to develop a hydrogen-based network [62]. The high pressure required to store large amounts of hydrogen that demand high pressure and therefore high consumption of energy is the main challenge to overcome to use hydrogen as fuel in daily life completely. Some hydrogen storage solutions have faced problems concerning materials cost or high operating costs [63]. The use of pure gas hydrates to store hydrogen is impractical due to the extreme pressures (2 kbar) required to form. However, the pressure required to form hydrates can be decreased by two orders of magnitude by using promoters such as tetrahydrofuran (THF) which occupies the large cavity available in the hydrate structure and stabilize the material while the small cavity is occupied by the hydrogen [64]. Hydrogen hydrates could represent a clean, safe and affordable storage material for mobile applications [65]. According to Lee et al. hydrogen storage capacities in THF can be increased to 4 wt% at modest pressures by adjusting their composition to allow hydrogen and THF to enter the large and small cages whereas retaining low-pressure stability. They used watersoluble hydrate promoters and different small gas guests [66]. However, the main challenge to

store hydrogen in hydrates is the balance between the storage capacity and the conditions for mild pressure and temperature [2].

2.4 In situ deposits

Gas hydrates are considered a large energy resource since their discovery in the 1960's [67]. The amount of organic carbon in nature present in hydrated form is so large that is more than double that of the carbon in fossil fuels [68] as can be seen in Figure 8.



Figure 8. A comparison of energies in conventional hydrocarbons and hydrates. The distribution of organic carbon in Earth reservoirs is shown in gigatons (1015 tons) of carbon. 1 gigaton = 38.84 trillion ft3 (TCF) [123].

Methane from gas hydrates was originated from two processes. The first one is biogenetic methane, formed through the process of bacterial decomposition of organic matter. The second process is thermogenic methane, produced through the hydrocracking of sedimentary organic matter. Some countries are in the process of developing methods and technologies to exploit these reserves sustainably. In Japan, scientists were able to extract methane. They estimate to produce gas commercially within six years. This success is very remarkable since Japan imports all energy needs, making it the world's top importer of liquefied natural gas [69]. Scientists in Canada have proved to use methane, dissociating and collecting it from a hydrate reservoir using a closed-cycle heated water system [70]. However, further research in the use of methane from gas hydrates must be performed and focused on evaluating the potential risk of it to the environment since methane

could be released uncontrolled if the temperature of the planet rises [25]. In other words, in situ hydrate deposits could significantly contribute to global warming taking into account that methane is 21 times more harmful to the ozone layer than carbon dioxide [71]. As methane is released because of global warming the temperature of the planet could increase even more causing a vicious cycle called the runaway greenhouse effect [25].

2.5 Phase equilibria

The full understanding of gas hydrates is crucial to develop and propose new technology and methods applicable to tackle global warming, improvements in storage and transport of natural gas and hydrate related industries [25]. Research in the field has focused on studying the methods for the calculation of phase equilibria and modeling. Since the discovery of gas hydrates, research has dedicated effort to determine the equilibrium conditions at which gas hydrates form and the suitable guest molecules. Thermodynamic equilibrium is reached when thermal, mechanical, chemical equilibrium coexist. Hydrate systems have three phases such as hydrate-liquid water-vapor (H-Lw-V). In Figure 9 can be seen the four phase diagram. Gases with critical temperatures lower than K_1 will not liquefy and will not reach a second quadruple point since they will retain their gaseous form or become supercritical. On the other hand, gases such as carbon dioxide and ethane that have higher supercritical temperatures will present a second quadruple point past K_1 where H-Lw-V-L guests interact while methane and nitrogen do not. In Figure 10 can be seen the phase diagram of methane.



Figure 9. Four phase diagram: hydrate (H), liquid water (L_w), vapor (V), ice (I) and liquefied guest (L). K_1 is a quadruple point where four phases interact: H-Lw-V-I. The dotted line and the existence of K_2 , are dependent on the thermodynamic conditions allowing the guest to liquefy. Therefore, K_2 is a possible second quadruple point where four phases interact: H-Lw-V-L. Hydrate formation region is favorable while hydrate free region is unfavorable [2].

Depending on the thermodynamic conditions, other phases like ice or liquefied gas can exist in the hydrate systems. Equilibrium conditions are determined using either the isothermal method and calculating the pressure or the isobaric method and calculating the temperature. Both methods work by increasing and adjusting one state parameter smoothly towards the hydrate dissociation conditions while monitoring the formation of hydrates. Sloan *et al.* have studied different hydrateliquid-vapor systems [2].

Due to the importance of gas hydrates, the development of models to predict hydrate equilibrium conditions has been crucial to understand the nature of gas hydrates significantly.

Van der Waals and Platteeuw published their work concerning a model to calculate the chemical potential in the hydrate phase and calculated the formation pressure for various gases [72]. This model was used as a basis by Parrish and Prausnitz to predict equilibria in multicomponent mixtures [73]. Kobayashi et al. combined classical thermodynamics with the Van der Waals and Platteeuw's work to predict hydrate formation conditions [74]. The Trebble-Bishnoi equation of state can be used to calculate the vapor and liquid phases [75] while the Van der Waals and Platteeuw model are used to describe the hydrate phases. Peng-Robinson equation of state also

can be used to describe thermodynamic properties accurately. A flash calculation can be used to solve a hydrate forming system at equilibrium [25]. Bishnoi *et al.* [76] were the first to perform complete system calculations and predictions. These calculations solve phase equilibria and stability equations for multicomponent systems. Models such as the non-random two liquid model (NRTL) [77] or statistical associating fluid theory (SAFT) [78] were developed to predict the features of complex fluid mixtures. Normally, hydrate phase models use a variant of the Van der Waals-Platteeuw model. According to this model, the fugacity of the water in the hydrate phase is equal to the fugacity of water in the liquid phase. Recently, some studies have focused on the solubility of the gas hydrate former in the liquid-hydrate region throughout the hydrate-liquid-vapor equilibrium line.



Figure 10. Phase diagram showing boundary between free methane gas and methane hydrate for a pure water and pure methane system [124].

2.6 Kinetics of hydrate formation

Thermodynamic conditions must be reached above equilibrium to induce hydrate growth [79] as illustrated in the hydrate formation region in Figure 9. The system reaches equilibrium when the gas is consumed, or the three-phase vapor liquid-hydrate is achieved [79]. These equilibrium conditions are maintained along the experiments to study their effects. The setup used to study hydrate formation, growth, and kinetics is equipped with a chiller to keep the temperature constant, stirrer, windows for visual observation, and pressure and temperature gauges. Figure 11 illustrates a gas consumption curve that can be obtained using a setup recently mentioned. In kinetics, the study of dissolution, induction, nucleation, saturation, and growth, is crucial to the understanding of hydrates. In the first part of the hydrate formation process, the gas is dissolved up to the point of saturating the liquid [79]. Following this, the liquid is at the three-phase equilibrium, and further dissolution of the gas forces the system into the hydrate-liquid region. Subsequently, the induction period is where the system is supersaturated [2]. In this region, the gas keeps dissolving and increases the driving force to create a new phase.

In general, the gas hydrate formation process is divided in two: nucleation and growth. These two processes are separated by the turbidity point.



Figure 11. Gas consumption curve measured during a hydrate formation experiment [125].

2.6.1 Nucleation

Nucleation is probably the most important stage in understanding the process of gas hydrate crystallization. Moreover, its grasp is essential to have either kinetic inhibition or promotion in the process [80]. During the nucleation phase, hydrate nuclei are formed in a supersaturated aqueous solution. The nucleation process is concluded by the presence of critical sized, stable hydrate nuclei. On the other hand, in the growth phase, the hydrate nuclei grow as solid hydrate crystals. The Induction period is defined as the duration of the nucleation phase [81]. Nucleation is based on the formation and decomposition of clusters of gas molecules as a result of concentration fluctuations. Each supersaturated solution has a critical cluster (critical nucleus) that is in equilibrium with the system and has the same probability of growth as of disintegration. If the size of a cluster is less than the critical size, its probability of decomposition is high whereas if the opposite occurs, the cluster grows spontaneously. Hence, the critical size is a barrier the clusters must overpass to grow as solid crystal. According to Makagon et al. [82], Vysniauskas et al. [83], and Englezos *et al.* [84], the clustering process is the precursor of hydrate nuclei formation. The size at which the hydrate nuclei is stable is known as critical size, was first calculated by Englezos et al. They derived an expression to calculate the free energy of a hydrate nuclei for the growth of hydrate particles after the nucleation process [81].

There are two types of nucleation: homogeneous and heterogeneous [79]. Homogeneous nucleation takes place in the bulk of a phase while heterogeneous nucleation occurs on a surface in contact with the bulk. This contact can decrease the energy barrier to form crystals by reducing the surface area of a new interface [85]. Heterogeneous nucleation is nearly exclusively present in macroscopic-scale systems [80].

The gas hydrate memory effect [86] is a reduction in the induction time where hydrates have previously been formed [67]. This effect is caused when the structure of system impurities is modified to conform the crystal structure. Hence, the next time hydrates are formed, they have a template for their crystal structure. However, this effect is controversial since some authors [87][88][89] state that the memory effect is, in reality, the presence of hydrate nuclei in small quantities that did not disappear in the system when hydrates deformed. For this reason, gas hydrates are formed faster than the first time.

In Figure 11 can be seen the formation of stable gas hydrates that is indicated when the turbidity point is achieved by a spike in temperature due to the exothermic nature of the crystal growth [2].

2.6.2 Growth

The formation of stable hydrate crystals is the beginning of the growth phase, along with a temperature increase when the phase change that is exothermic goes from liquid to solid. The hydrate phase contains up to 15 mole % of gas, two orders of magnitude greater than methane solubility, to have the sufficient driving force or a significant amount of gas molecules in the system to cross the multiple phases and interphases to reach the hydrate surface [2]. In Figure 12 can be seen the three phase diagram where the gas molecules cross from the initial gas phase to the final hydrate phase. Gas hydrates are studied in a stirred batch and temperature controlled crystallizer to ensure parameters such as heat and mass transfer do not affect gas hydrate growth.



Hydrate former mole fraction

Figure 12. Diagram of gas transfer during hydrate growth [126].

Even though the thermodynamics of gas hydrates have been widely studied for more than 30 years (van der Waals and Platteeuw, 1959; Parrish and Prausnitz, 1972; Ng and Robinson, 1976; John et al., 1985) kinetics of gas hydrates have been recently researched. Vysniauskas and Bishnoi (1983, 1985) were among the first scientists to publish information on the kinetics of gas hydrates

formation. They used methane and ethane in their studies and developed a semi-empirical model to correlate the experimental data which were obtained by contacting gas with water at temperatures above 0 °C. Their study tried to describe quantitatively and model the formation kinetics of gas hydrates. Vysniauskas and Bishnoi concluded from their studies that the appearance of nuclei causes hydrate formation and consequent growth [83]. Growth is in function of the temperature, pressure, interfacial area and the degree of super-cooling. The induction period is affected by the history of the water, but it does not have an effect on the growth of the nuclei. Kim et al. (1987) have also studied the kinetics of gas hydrates decomposition [90].

During the transfer of the gas from the vapor phase to the hydrate phase, it faces four resistances as can be seen in Figure 12. The V-Lw interface consists of resistances to mass transfer on the vapor side in addition to the liquid side. The resistance on the vapor side is negligible compared to that of the liquid side according to a scaling analysis [91]. The H-Lw interface consists of resistances to mass transfer on the liquid side and also the resistance to enclathration, also known as the reaction resistance. Scaling analysis at the H-Lw interface shows that the resistance to mass transfer is negligible compared to the reaction resistance for carbon dioxide [92] and methane systems [93].

According to Englezos, [90] the difference between the fugacity of the dissolved gas at experimental temperature and pressure, and the fugacity of the dissolved gas at experimental temperature in the three-phase equilibrium pressure is defined as the driving force. Skovborg and Rasmussen defined the driving force as the difference between the mole fraction of the guest gas in the water phase at the water-gas interface in equilibrium in the vapor phase at equilibrium conditions, and the mole fraction of guest gas in the bulk water phase in equilibrium with the hydrate phase at equilibrium conditions. They concluded that the hydrate formation rate is mass transport limited and therefore independent of the total particle surface area. They assumed for their model that the transport of guest gas molecules from the vapor phase to the liquid water phase is the rate-determining step in the overall hydrate formation process [94].

Bergeron and Servio proposed a new driving force for hydrate growth. This driving force simplifies previous hydrate growth models designed to calculate the reaction rate constant of hydrate formation and eradicate the use of the resistance at the V-Lw interface. Their model is practical since the bulk liquid mole fraction is directly used instead of the guest gas mole fraction at the V-Lw interface [95].

The development of kinetic models to predict hydrate growth was proposed by Glew and Hagget [96]. The relation between hydrate formation rate and the temperature difference between the reactor and cooling bath was based on their model. Some models include temperature and fugacity [90] to calculate driving forces and concentration [94]. Some of these kinetic models have difficulty characterizing the mass transfer across the V-Lw interface.

2.7 Thermodynamics of hydrate formation

Thermodynamics of gas hydrates focuses on measuring the pressure-temperature conditions at which three-phases, hydrate, liquid water, and vapor are in equilibrium. These three-phase equilibrium conditions have been measured in different gas species and mixtures.

In 1885, Roozeboom made the first pressure-temperature plot for SO₂ hydrate, similar to that in Figure 13 for several components of natural gases.



Figure 13. Phase diagrams for some natural gas hydrocarbons that form hydrates. Q1 lower quadruple point. Q2 upper quadruple point [2].

The hydrate region is to the left of the three-phase lines (I-H-V, L_W-H-V, L_W-H-L_{HC}); the liquid water, ice, and the guest gas as vapor or liquid phases exist to the right.

In 1946, Deaton and Frost were the first scientists to perform experiments to determine the hydrate forming conditions. They used the isothermal pressure-search method that consists of setting the system at a defined temperature while slowly increasing the pressure until hydrates are formed. The equilibrium pressure is that at which hydrates are formed at that specific temperature when the system is left at equilibrium for an amount of time that in theory can be infinite. However, in reality, hydrates require a driving force to form. If the hydrate crystallizer is set at the exact equilibrium pressure, they will not form. The driving force is the potential for the system to form hydrates. To exemplify this concept, consider the fact that methane hydrates form at 8.5 °C and a pressure of 6 MPa. If the system is exposed to these conditions, hydrates will never form. It is because no driving force is present at equilibrium conditions.



Figure 14. Three-phase equilibrium curve for hydrate-liquid water-methane gas [127]

Even though thermodynamics state that hydrates are present under these conditions, their formation will never take place without the presence of a driving force. If the pressure is increased by 10 kPa to 6,010 kPa keeping the other conditions constant, the driving force would be 10 kPa. Now in the system 10 kPa act as a driving force. While 10 kPa is a small driving force, hydrates have the potential to form. However, gas hydrates can take a long time to form and it is difficult to predict. The use of a small driving force triggers large formation times, thus it is not feasible for practical purposes. Nevertheless, if the driving force is increased by 1000 kPa, the time of formation of hydrates is decreased, and hydrates can form in a relatively short time. This time, the driving force is high enough to form hydrates faster than using 10 kPa. Once hydrates are formed, the pressure of the system can be adjusted to the equilibrium pressure. This pressure is achieved by slowly decreasing it until hydrate deformation is observed. At this pressure and temperature, the equilibrium conditions are registered, and the procedure is repeated for different temperatures until a phase diagram is plotted as illustrated in Figure 14 and Figure 15. Moreover, this phase

diagram can be obtained by using the pressure, keeping it constant and adjusting the temperature of the crystallizer. However, this method is time-consuming due to the thermal equilibrium all the system has to reach.



Figure 15. Three-phase equilibrium curve for hydrate-liquid water-carbon dioxide gas [128].

2.8 Semi-clathrates

A special type of hydrate promoting compound known as semi-clathrate was discovered by Fowler et al. in 1940 [97]. Its host structure is not exclusively composed of water molecules [98]. These semi-clathrates are formed by water molecules and by different types of compounds, some of the most researched are the quaternary ammonium salts (QAS) [99] such as tetrabutylammonium chloride (TBAC), or tetrabutylammonium bromide (TBAB). Semi-clathrate hydrates share many physical properties to gas hydrates. Semi-clathrates hydrates differ from gas hydrates in that they form at a lower pressure or even at atmospheric pressure for a given temperature, and that the semi-clathrate hydrates can form both in the absence and in the present of a guest molecule that would otherwise be a gas or volatile liquid. Such a hydrate is called a semi-clathrate hydrate because a part of the cage structure is broken to encage the large tetra-nbutylammonium molecule as illustrated in Figure 16. In this semi-clathrate hydrate structure, both the tetra-n-butylammonium cations (TBA⁺) and the guest molecule are located in the center of tetragonal cages, while the halide anions (Br⁻, Cl⁻, or F⁻) form a selective framework with water molecules by H-bond [35]. Two tetrakaidecahedron and two pentakaidecahedra conform the structure where the Tetra-n-butylammonium cations are located at the center of four cages, while the dodecahedral cages can be occupied by small molecules such as methane or carbon dioxide as shown in Figure 16 by the shaded areas.

Empty pure gas hydrates structures cannot form in the absence of a gas molecule [100]. In the semi-clathrate hydrate structures, the tetrabutylammonium cations (TBA⁺) are located in the center of tetragonal cages as a guest molecule, while the halide anions (Cl⁻, Br⁻) form a framework with water molecules through hydrogen bonding [58]. Guest gases participate in the cage structure and occupy cages. By contrast, in gas hydrates, the guest molecule is required to form the lattice through weak Van der Waals interactions [26]. This configuration lends great thermal stability to the structure, providing TBAC semi-clathrates forming at a temperature of 3 °C for 5-wt%, 9 °C for 10-wt% and 11 °C for 15-wt% at atmospheric pressure [35], [101]–[103]. Garcia and Clarke [104] found that semi-clathrates form on average at one tenth of the pressure required to form gas hydrates.



Figure 16. Tetra-n-butylammonium bromide semi-clathrate hydrate structure [106]

The crystallography of semi-clathrate structures was studied by X-ray before those of pure clathrates [105]. Clathrate hydrate structures are classified by their hydration number, the number of water molecules per molecule of hydrate [2]. There are five crystal structures of the TBAB semi-clathrate in systems under 60 wt%, with hydrate numbers of 24, 26, 32, 36 and 38 [106]. Several studies have proved that these structures are stable at different weight fractions of TBAC [106][107]. The variety of TBAC semi-clathrate structures can cause confusion about which structures are forming. Because TBAB semi-clathrates can be formed solely with water, the introduction of guest gases in the cages can complicate the comprehension of the crystal structure.

Shuanshi et al. [108] measured the phase equilibrium data for a gas mixture of CO_2/CH_4 using different QASs with a TBAC/TBAB mole fraction of 2.9×10^{-3} and temperatures from 7 °C to 18 °C and pressure from 0.6 MPa to 9 MPa. The study of Garcia et al. [100] presented a valuable database for the thermodynamic equilibrium conditions of TBAB and TBAC semi-clathrates using six different pure gases. Mingjun et al. [109] tested a combination of two thermodynamic promoters THF and TBAB and observed a decrease in equilibrium pressure compared to the addition of solely THF or TBAB. In their work, Zhong et at. [110] studied a gas mixture of CH₄, N₂, and O₂ in the presence of TBAB, also demonstrating that semi-clathrates hydrates form at a lower pressure than gas hydrates for this gas mixture.

All the studies above have performed valuable research and have concentrated on phase equilibria but have not reported any measurement of the liquid mole fraction for semi-clathrate systems.

2.8.1 Promoters

Some of the limitations of gas hydrates are high pressure and low temperature required to form, and the slow formation kinetics that has triggered the lack of large scalability [111]. Research has been carried out to promote growth using chemical promoters to phase these limitations. These additives promote hydrate nucleation by reducing the surface tension of the gas-liquid interface and increasing the gas solubility and diffusion coefficient in the liquid phase [112]. Moreover, these additives increase the rate of hydrate formation. Gas hydrate promoters are used as chemical additives in hydrate formation processes. The gas hydrate promoter reduces the required hydrate formation pressure and increases the formation rate and temperature. In addition, it modifies the

selectivity of hydrate cages to absorb various gas molecules [51]. There are two types of promoters, kinetics and thermodynamic promoters. The former are molecules that have the effect to accelerate hydrate formation without changing the hydrate equilibrium conditions. These promoters are generally surfactants such as sodium dodecyl sulfate (SDS) [113]. The latter typically consist of organic compounds such as cyclic ethers or quaternary ammonium salts, which change the equilibrium conditions allowing higher temperatures or lower pressures. Thermodynamic promoters make hydrate formation more energetically favorable. Examples of these additives are tetrahydrofuran (THF) and cyclopentane, which integrate into larger cages in the hydrate structure and therefore assist the storage of smaller gas molecules such as methane or carbon dioxide in the empty cages [114]. A schematic representation of a thermodynamic promoter such as TBAB acting in a semi-clathrate hydrate structure is illustrated in Figure 16.

2.9 Research Objectives

The main objectives of this work were to study the phase equilibrium relations for gases in water in the presence of gas hydrates. First, the methane-water system in the presence of the thermodynamic promoter TBAC was studied to generate accurate equilibrium measurements of the system. Afterward, equilibrium measurements were undertaken for the carbon dioxide-water-TBAC system. In addition, the measurement of liquid mole fraction for methane-water-TBAC and carbon dioxide-water-TBAC systems were undertaken. Overall, these experiments were performed to evaluate semi-clathrates as an alternative to store and transport gases of economic and environmental importance.

This thesis is the first study to report experimental liquid mole fraction results obtained through sample extraction at three-phase equilibrium for the $CO_2/CH_4 + TBAC + H_2O$ system. In literature, reports of liquid mole fraction measurements are relatively scarce even though they are essential in gas hydrate applications. Semi-clathrates hydrates can store large amounts of gas in a relatively small volume [115], much of the interest in these structures has arisen from their potential applications in a vast variety of industries.

3. Materials and Methods

3.1 Experimental setup

Reactor

The reactor is a high-pressure crystallizer constructed of 316-stainless steel resistant to pressures up to 20 MPa. The reactor has a 76.2 mm internal diameter, 44.4 mm wall thickness and a volume of 550 ml. The reactor lid is 47 mm thick and is sealed to the body of the reactor using six ½ inch rods and a Buna O-ring. The reactor has two circular polycarbonate viewing windows. The reactor is equipped with a mount Dyna/Mag magnetic mixer with a control for speeds up to 2500 rpm. The reactor has five 1/8 inch female NPT ports, two of these occupied by Omega high accuracy RTD probes for temperature measurement and the remaining three ports are used for sampling, purging and loading the reactor with gas. In Figure 19 can be seen the reactor as part of the setup.

Experimental equipment

The experimental equipment used is illustrated in Figure 17. A Baumann 51000 series low flow control valve is connected to the reactor. The absolute pressure in the reactor is measured using 3051S Rosemount pressure transducers for pressure from 0 MPa to 14 MPa and an accuracy of ± 0.065 % of the span. The reactor is submerged in an insulated bath of a glycol-water mixture. The bath is maintained at constant temperature employing a chiller that circulates the cooling solution through a copper coil. Omega RTC probes are used to measure the temperature inside the reactor.



Figure 17. Experimental equipment.

Data collection and additional equipment

The readings throughout the experiments were recorded using NI LabVIEW software. The sampling port is equipped with a Norman 4200 filter that retains particles larger than 20 nm in diameter. The filter prevents the liquid sample from containing gas hydrates and skewing the measurement. The vessel to collect 10 ml samples is made of stainless steel.

A Chandler gasometer, shown in Figure 18, is used to measure the volume of gas contained in the liquid sample when it is left to equilibrate at room temperature and atmospheric pressure. The gasometer consists of two Pyrex chambers of 1000 ml and 2000 ml. A floating piston in each chamber is connected to a rack and pinion that allows for the piston to be positioned through the use of control knobs. Digital volume meters are used to register in cubic meters the expansion of the sample into the gasometer. The temperature inside each chamber is measured using Omega thermocouples. The accuracy of the volume readings is 0.2 %. For weighting, a Denver Instruments S-4002 is used with an uncertainty of \pm 0.01 g.



Figure 18. Chandler digital gasometer

3.2 Materials

Tetra-n-butylammonium chloride (TBAC) was acquired from Sigma-Aldrich at a concentration \geq 97.0 wt %. Carbon dioxide gas (99.995%) and methane gas (99.99%) were both purchased from MEGS Inc. Reverse Osmosis (RO, 0.22 µm filter, conductivity of 10 µS, total organic content <10 ppb) water was treated and obtained in-house.

3.3 Procedure for equilibrium experiments

Experiments were carried out at different temperatures and pressures as reported in Table 2 and Table 3. Measurements were performed in triplicate for each temperature. For both gases, the concentrations of TBAC used were 5-wt%, 10-wt%, and 15-wt%. Initially the temperature of the bath was set and wait for the system to equilibrate. Afterwards, the reactor was rinsed four times with reverse osmosis water. Following this, 450 ml of reverse osmosis water was loaded into the reactor. The system was pressurized to 1 MPa with the desired gas allowing time to mix and then depressurizing to atmospheric pressure with the tested gas, and purged twice to clean the output gas lines and purge the 450 ml of water. Following this, the reactor was loaded with the desired gas and test solution; the pressure was brought above the equilibrium according to literature data [100][116][117]. Stirring was started, and once hydrates formed (verified visually as crystals appear suspended in the solution), the pressure was decreased near the equilibrium pressure. The system was left to equilibrate under stirring for at least 12 hours. During that time, pressure and temperature (± 0.5 K) were stable at the time of sample removal. The system was considered stable if pressure and temperature fluctuated under these conditions for 12 hours.



Figure 19. Experimental setup

Before taking the sample, the stirrer was turned off, and the solution was allowed to stand for a few minutes for the hydrates to sink. Four samples of 10 ml were taken in vessels and passed through a 20-nm high-pressure Norman filter. Prior to sampling, the vessels were weighed, vacuumed and conditioned at the same temperature of the glycol bath to ensure thermal consistency. The first sample was discarded for cleaning purpose while the remaining were analyzed in a gasometer. The samples were left for 1.5 hours connected to the gasometer until equilibrium was reached to depressurize the gas. The atmospheric pressure, temperature, and gas volume were registered. Following this, the liquid was removed from the vessel, and the TBAC equilibrium liquid concentration was measured in a refractometer. Finally, the vessels were washed, and the process could be repeated at different concentrations and experimental conditions. The overall procedure for equilibrium measurements is illustrated in Figure 19.

4. Results and Discussions

4.1 Solubility calculations

The phase equilibrium conditions, the molar fraction of the guest gas and the TBAC are reported in Table 2 for methane and Table 3 for carbon dioxide. The experiments were performed at the three-phase equilibrium. Figure 19 shows the measurement procedure and sample analysis. It was assumed that no TBAC was present in the gas phase when using the gasometer. The guest gas was assumed to be ideal for ambient conditions. Water pressure was assumed to be the vapor pressure at room temperature and was calculated using the Antoine equation (1) taken from the NIST webbook [118]. The number of moles of all species was computed using the following equations (2-8).

$$\log_{10} P = A - \frac{B}{C+T}$$
(1)

$$n_{\rm T}^{\rm v} = \frac{{\rm V}\,{\rm P}}{{\rm R}\,{\rm T}} \tag{2}$$

$$n_{\rm w}^{\rm v} = \frac{P_{\rm H2O}^{\rm Vapor}}{p_{\rm amb}} n_{\rm T}^{\rm v}$$
(3)

$$n_g^v = n_T^v - n_w^v \tag{4}$$

$$n_{w}^{L} = \frac{x_{H_{2O}}^{L} * (m_{b} - n_{g}^{v} M_{g} - n_{w}^{v} M_{H_{2O}})}{M_{H_{2O}}}$$
(5)

$$n_{\text{TBAC}}^{\text{L}} = \frac{x_{\text{TBAC}}^{\text{L}} * (m_{\text{b}} - n_{\text{g}}^{\text{v}} M_{\text{g}} - n_{\text{w}}^{\text{v}} M_{\text{H2O}})}{M_{\text{TBAC}}}$$
(6)

The number of moles of guest gas remaining in the liquid phase was calculated using equation (8) and Henry's constant (7) reported in the NIST webbook [118].

$$k_{g} = k_{g}^{0} \exp\left(\frac{d(\ln k)}{d\left(\frac{1}{T}\right)} \left(\frac{1}{T} - \frac{1}{298.5}\right)\right)$$
(7)

$$n_g^L = k_g * P^{amb} * n_w^L * M_{H2O}$$

$$\tag{8}$$

The mole fractions were calculated once having the number of moles of each species and the total.

Uncertainty values for mole fractions were calculated using the following equations [119].

$$s = \sqrt{\frac{\sum_{k=1}^{n} (y_k - \bar{y})}{(n-1)}}$$
(9)

$$u = \frac{s}{\sqrt{n}} \tag{10}$$

Here y is a variable, \overline{y} is the average of a set of n values of y, s is the standard deviation and u is the standard uncertainty.

Table 2. Experimental V-L_W-H equilibrium data for temperature T, pressure P, methane mole fraction X_{CH4} and TBAC mole fraction X_{TBAC} with standard uncertainties $u(X_{CH4})$ for the system CH₄-TBAC-water. CI: confidence interval.

TBAC loading concentration/wt%	T/K	P/MPa	$X_{CH4}\left[x10^3\right]$	95% CI [x10 ³]	$u(X_{CH4}) \left[x10^3\right]$	X _{TBAC} [x10 ³]	$u(X_{TBAC}) [x10^3]$
5	280.0	0.827	0.3705	0.07	0.0222	3.1973	0.111
5	282.1	1.680	0.6489	0.09	0.0306	3.3561	0.070
5	284.1	2.550	0.8082	0.08	0.0279	3.4589	0.040
5	285.2	4.225	1.2272	0.15	0.0355	3.5872	0.026
5	286.1	4.750	1.5437	0.21	0.0499	3.1758	0.124
10	284.1	1.034	0.5166	0.15	0.0360	6.7802	0.037
10	285.1	1.650	0.9376	0.14	0.0341	6.5490	0.072
10	286.1	2.082	0.8930	0.23	0.0551	6.6168	0.114
10	287.2	3.019	1.0809	0.22	0.0524	6.7063	0.099
10	288.2	3.900	1.8818	0.24	0.0576	6.7292	0.075
15	286.0	1.050	0.4905	0.09	0.0226	10.7469	0.032
15	287.0	1.530	0.6134	0.17	0.0413	10.6769	0.141
15	288.0	1.995	0.6572	0.11	0.0267	11.4986	0.089
15	289.1	2.964	1.0945	0.13	0.0321	11.0558	0.131
15	290.2	3.500	0.9735	0.05	0.0136	11.4128	0.099

TBAC loading concentration/wt%	T/K	P/MPa	$X_{CO2}\left[x10^3\right]$	95% CI [x10 ³]	$u(X_{CO2}) [x10^3]$	$X_{TBAC} \left[x10^3 \right]$	$u(X_{TBAC}) [x10^3]$
5	277.2	0.326	4.6765	1.87	0.436	3.679	0.027
5	278.0	0.500	6.3256	1.47	0.342	3.554	0.055
5	279.0	0.863	9.1423	0.54	0.128	3.414	0.038
5	280.1	1.683	14.329	2.97	0.691	3.551	0.042
5	281.0	2.488	18.756	3.78	0.879	3.366	0.049
10	281.3	0.189	2.2207	0.09	0.022	6.600	0.039
10	282.1	0.309	3.1700	0.31	0.073	6.609	0.044
10	283.0	0.523	4.8848	0.40	0.095	6.494	0.063
10	284.2	0.923	7.8007	0.52	0.122	6.321	0.001
10	285.1	1.417	10.876	1.00	0.234	6.370	0.017
15	284.1	0.160	1.4210	0.42	0.098	10.106	0.112
15	285.1	0.258	2.1817	0.27	0.063	10.473	0.017
15	286.2	0.482	3.8824	0.37	0.087	10.935	0.099
15	287.1	0.788	6.0304	0.13	0.031	11.101	0.014
15	288.2	1.378	9.5268	0.25	0.058	10.902	0.047

Table 3. Experimental V-L_W-H equilibrium data for temperature T, pressure P, carbon dioxide mole fraction X_{CO2} and TBAC mole fraction X_{TBAC} with standard uncertainties $u(X_{CO2})$ for the system CO₂-TBAC-water. CI: confidence interval.

4.2 Equilibrium measurements

Experiments were conducted at the three-phase equilibrium. For methane, the conditions ranged from 280 to 290 K and 0.82 to 4.7 MPa and for carbon dioxide from 276 to 288 K and 0.16 to 2.8 MPa. Experimental equilibrium pressure at various temperatures and TBAC concentrations can be found in Figure 20 for methane and Figure 21 for carbon dioxide. In both figures, equilibrium conditions in the absence of TBAC [2] are plotted to illustrate its effect of decreasing the pressure and increasing the temperature of hydrate formation.



Figure 20. Experimental V-L_W-H equilibrium pressure at various temperatures and TBAC concentration for the system CH₄-H₂O-TBAC. This work: 5-wt%, 10-wt%, 15-wt%. Literature: 0-wt% [2].

In Figure 20 can be seen the experimental equilibrium for the CH₄-H₂O-TBAC system. This graph illustrates the conditions at which semi-clathrate hydrates are formed at different concentrations at 5-wt %, 10-wt%, and 15-wt %. In this graph can be proved what is reported in literature in the absence of TBAC, that the gas hydrates equilibrium pressure is higher than that of the semi-clathrate hydrates. 5.2 MPa of pressure are required to form gas hydrates at 280 K contrasted with the 0.82 MPa needed at the same temperature when using 5-wt % TBAC. At the three different concentrations, the increase of temperature in the reactor can be achieved by increasing the pressure that follows an exponential trend. For 5-wt % this trend has an r^2 value of 0.987 to the equation $y = 1 \times 10^{-35} e$ (0.2869x). The pressure ranged from 0.8 MPa at 280 K to 4.7 MPa at 286 K. For 10-wt %, the equilibrium pressure follows an exponential trend with an r² value of 0.987 to the equation $y = 2x10^{-39} e (0.3135x)$. The pressure ranged from 1 MPa at 284 K to 3.9 MPa at 288 K. Lastly, for the concentration of 15-wt %, the equilibrium pressure also follows an exponential trend with an r² value of 0.985 to the equation $y = 1x10^{-37} e (0.2972x)$ and the pressure ranged from 1 MPa at 286 K to 3.5 MPa at 290 K. Comparing the equilibrium conditions of the three different concentrations, an increase of 6 K in the reactor can be achieved by keeping the pressure and liquid mole fraction relatively constant while increasing the TBAC concentration from 5-wt% (0.8 MPa, 280 K, X_{CH4} 0.37x10⁻³) to 15-wt% (1 MPa, 286 K, X_{CH4} 0.49X10⁻³).



Figure 21. Experimental V-L_W-H equilibrium pressure at various temperatures and TBAC concentration for the system CO₂-H₂O-TBAC. This work: 5-wt%, 10-wt%, 15-wt%. Literature: 0-wt% [2].

In Figure 21 can be seen the experimental equilibrium for the CO_2 -H₂O-TBAC system. This graph illustrates the conditions at which semi-clathrate hydrates are formed at different concentrations at 5-wt %, 10-wt%, and 15-wt %. This graph can prove what is reported in the literature in the absence of TBAC, that the gas hydrates equilibrium pressure is higher than that of the semi-clathrate hydrates. 2 MPa of pressure are required to form gas hydrates at 277.5 K contrasted with the 0.32 MPa needed at the same temperature when using 5-wt % TBAC. At the three different concentrations, the increase of temperature in the reactor can be achieved by increasing the pressure following an exponential trend. For 5-wt % this trend has an r² value of 0.996 to the equation $y = 5x10^{-66}e^{-0.5384x}$. The pressure ranged from 0.3 MPa at 277 K to 2.4 MPa at 281 K. For 10-wt %, the equilibrium pressure follows an exponential trend with an r² value of 0.994 to the equation $y = 2x10^{-66} e (0.5329x)$. The pressure ranged from 0.18 MPa at 281 K to 1.4 MPa at 285 K. Lastly, for the concentration of 15-wt %, the equilibrium pressure also follows an exponential trend with an r² value of 0.998 to the equation $y = 8x10^{-68} e (0.5374x)$ and the pressure ranged from 0.16 MPa at 284 K to 1.3 MPa at 288 K. Comparing the equilibrium conditions of the three different concentrations, an increase of 8 K in the reactor can be achieved by keeping the pressure relatively constant and increasing the TBAC concentration from 5-wt% (0.3 MPa, 277 K) to 15-wt% (0.25 MPa, 285 K).



Figure 22. Experimental V-L_W-H equilibrium CH₄ solubilities at various temperatures and TBAC concentrations for the system CH₄-TBAC-H₂O. Confidence interval 95 %.

Liquid mole fraction measurement is essential to evaluate the capacity of the system of store gases. In Figure 22 can be seen the experimental three-phase equilibrium solubilities of methane at various temperatures and TBAC concentrations. Measurements were performed in triplicate for each temperature. Student's t-distribution was used with a confidence interval of 95 %. In Table 2 can be seen the confidence intervals. In the graph above, no overlap of error bars is observed among the three different TBAC concentrations. For 5-wt %, the error bars are significantly narrow at low temperature when the pressure is low as well. However, they increase when both temperature and pressure increase. Unlike 5-wt %, for 10-wt % error bars are approximately equals between them. For 15-wt % error bars are completely different, their behavior is not consistent as observed with the other TBAC concentrations. Comparing the equilibrium conditions of the three different concentrations, an increase of 4 K in the reactor can be achieved at the same time the mole fraction is maintained relatively constant, by increasing the TBAC concentration from 5-wt % (4.2 MPa, X_{CH4} 1.22x10⁻³ at 285 K) to 15-wt% (2.96 MPa, X_{CH4} 1.09x10⁻³ at 289 K). The results above in better operating conditions regarding energy consumption due to the decrease in pressure while retaining the storage capacity. At a fixed temperature of 286 K, equilibrium was achieved for the three different concentrations: 5-wt % (4.7 MPa, X_{CH4} 1.5x10⁻³), 10-wt% (2 MPa, X_{CH4} 0.8x10⁻³) and 15-wt% (0.49 MPa, X_{CH4} 0.49x10⁻³) with a pressure reduction of hydrate formation as TBAC concentration increases while reducing the mole fraction.



Figure 23. Experimental V-L_W-H equilibrium CO_2 solubilities at various temperatures and TBAC concentrations for the system CO_2 -TBAC-H₂O. Confidence interval 95 %.

Knowledge of liquid phase composition, most particularly with respect to the guest gas, is essential for developing kinetic models for reactor design [95]. In Figure 23 can be seen the experimental three-phase equilibrium solubilities of carbon dioxide at various temperatures and TBAC concentrations. Measurements were performed in triplicate for each temperature. Student's t-distribution was used with a confidence interval of 95 %. In Table 3 can be seen the confidence intervals. In the graph above, no overlap of error bars is observed among the three different TBAC concentrations. The exponential trend for mole fraction is observed in the three concentrations. For 5-wt %, the error bars are significantly wide except for 279 K. Unlike 5-wt %, for 10-wt % error bars are narrow and approximately equals between them. The confidence intervals increase as does the temperature and pressure. For 15-wt % error bars are relatively similar and narrow, their behavior is more consistent as observed with the other TBAC concentrations. Comparing the equilibrium conditions of the three different concentrations, an increase of 9 K in the reactor can be achieved and keeping the mole fraction relatively constant, by increasing the TBAC concentration from 5-wt % (0.86 MPa, X_{CO2} 9.1x10⁻³ at 279 K) to 15-wt% (1.37 MPa, X_{CO2} 9.5x10⁻ ³ at 288 K). The results above in better operating conditions in terms of energy consumption due to the increase in temperature, thus less cooling demand while retaining the storage capacity. At a fixed temperature of 281 K, equilibrium was achieved at two different concentrations, either 5-wt % (2.4 MPa, X_{CO2} 18.7x10⁻³) and 10-wt% (0.18 MPa, X_{CO2} 2.2x10⁻³) or 10-wt % (0.9 MPa, X_{CO2}

7.8x10⁻³) and 15-wt% (0.16 MPa, X_{CO2} 1.42x10⁻³) with a pressure reduction of hydrate formation as TBAC concentration increases while reducing the mole fraction.



Figure 24. Experimental V-L_W-H equilibrium pressure and liquid mole fraction for the system CH₄-H₂O-TBAC.

In Figure 24 can be seen the experimental three-phase equilibrium that relates pressure and liquid mole fraction for the methane-water-TBAC system. In this graph can be observed a linear trend in the three concentrations which is more noticeable for 5-wt%. When it comes to relating pressure and mole fraction, it is remarkable how some points in the graph from different concentrations are close between them. Analyzing three different pairs of points that almost overlap, it can be observed that they have almost the same equilibrium conditions even though they have different temperatures and TBAC concentrations. Taking point A at 5-wt % (282 K, $X_{CH4} 0.64x10^{-3}$ and 1.6 MPa) and point A' at 15-wt % (287 K, $X_{CH4} 0.61x10^{-3}$ and 1.5 MPa) it can be said that the liquid mole fraction of the guest gas is not a strong function of pressure but of temperature and TBAC concentration of TBAC while keeping the mole fraction and pressure constant. Similar comparison can be done between point B at 10-wt % (284 K, $X_{CH4} 0.51x10^{-3}$ and 1.03 MPa) and point B' at 15-wt % (286 K, $X_{CH4} 0.49x10^{-3}$ and 1.05 MPa). Additionally, point C at 10-wt % (287 K, $X_{CH4} 1.08x10^{-3}$ and 3.01 MPa) and point C' at 15-wt %

(289 K, X_{CH4} 1.09x10⁻³ and 2.96 MPa). There are fifteen different measurements in the graph illustrated in Figure 24. For this research, these points tend to be close to each other at low pressures below 3 MPa, but these similarities at different TBAC concentrations are dispersed as the pressure increases. At higher pressures, the temperature effect on the mole fraction is stronger.



Figure 25. Experimental V-L_W-H equilibrium pressure and liquid mole fraction for the system CO₂-H₂O-TBAC.

In Figure 25 can be seen the experimental three-phase equilibrium that relates pressure and liquid mole fraction for the carbon dioxide-water-TBAC system. In this graph can be observed a strong linear trend in the three concentrations. For 5-wt %, the trend has an r^2 value of 0.996 to the linear equation y = 0.1499x - 0.0774. For 10-wt %, the trend has an r^2 value of 0.997 to the linear equation y = 0.1411x - 0.145. For 15-wt %, the trend has an r^2 value of 0.994 to the linear equation y = 0.1543x - 0.471. The linear trends of these three equations shows a strong relation between TBAC concentration, CO₂ liquid mole fraction, temperature and pressure. When it comes to relating pressure and mole fraction, it is remarkable how some points in the graph from different concentrations and equilibrium conditions are close between them in terms of liquid mole fraction values. Analyzing four different pairs of points, it can be observed that they have almost the same liquid mole fraction values even though they have different temperatures, pressures, and TBAC concentrations. Taking point A at 10-wt % (281 K, X_{CO2} 2.22x10⁻³ and 0.18 MPa) and point A' at 15-wt % (285 K, X_{CO2} 2.18x10⁻³ and 0.25 MPa) it can be said that the liquid mole fraction of the

guest gas is not a strong function of pressure but of temperature and TBAC concentration. In this comparison, the temperature of the reactor can be increased 4 K by increasing the concentration of TBAC 5-wt % while keeping the mole fraction significantly constant and pressure slightly variable. A similar comparison can be done between point B at 5-wt % (277 K, $X_{CO2} 4.67 \times 10^{-3}$ and 0.32 MPa) and point B' at 10-wt % (282 K, $X_{CO2} 4.88 \times 10^{-3}$ and 0.52 MPa). Moreover, point C at 5-wt % (278 K, $X_{CO2} 6.32 \times 10^{-3}$ and 0.5 MPa) and point C' at 15-wt % (287 K, $X_{CO2} 6.03 \times 10^{-3}$ and 0.78 MPa). Additionally, point D at 5-wt % (279 K, $X_{CO2} 9.14 \times 10^{-3}$ and 0.86 MPa) and point D' at 15-wt % (288 K, $X_{CO2} 9.52 \times 10^{-3}$ and 1.37 MPa). There are fifteen different measurements in the graph illustrated in Figure 25. For this research, these points tend to be close to each other at low pressures below 1 MPa, but these similarities at different TBAC concentrations are dispersed as the pressure increases. At higher pressures, the temperature effect on the mole fraction is even stronger.

5. Conclusions

Equilibrium conditions and solubility of the CH₄-TBAC-H₂O and CO₂-TBAC-H₂O systems were measured in the presence of TBAC at concentrations of 5-10-15-wt%. For the methane system, the temperatures varied from 280-290 K while the corresponding pressure ranged from 0.8 MPa to 4.7 MPa and the liquid mole fraction ranged from 0.37×10^{-3} to 1.88×10^{-3} . Phase Equilibrium condition results show that the addition of TBAC from 0 to 5-wt % can reduce the hydrate formation pressure from 5.2 MPa to 0.82 MPa at 280 K. At the three different concentrations, the increase of temperature in the reactor can be achieved by increasing the pressure that follows an exponential trend. Comparing the equilibrium conditions of the three different concentrations, an increase of 6 K in the reactor can be achieved by keeping the pressure and liquid mole fraction relatively constant while increasing the TBAC concentration from 5-wt% (0.8 MPa, 280 K, X_{CH4} 0.37x10⁻³) to 15-wt% (1 MPa, 286 K, X_{CH4} 0.49X10⁻³). Moreover, an increase of 4 K in the reactor can be achieved at the same time the mole fraction is maintained relatively constant, by increasing the TBAC concentration from 5-wt% (4.2 MPa, mole fraction of 1.22x10⁻³ at 285 K) to 15-wt% (2.96 MPa, mole fraction of 1.09x10⁻³ at 289 K).

For the carbon dioxide system, the temperatures varied from 277-288 K while the pressures ranged from 0.32 MPa to 2.48 MPa and the liquid mole fraction ranged from 1.42×10^{-3} to 18.76×10^{-3} . Phase equilibrium condition results show that the addition of TBAC from 0 to 5-wt % can reduce the hydrate formation pressure from 2 MPa to 0.32 MPa at 277.5 K. At the three different concentrations, the increase of temperature in the reactor can be achieved by increasing the pressure that follows a strong exponential trend. Comparing the equilibrium conditions of the three different concentrations, an increase of 8 K in the reactor can be achieved by keeping the pressure relatively constant and increasing the TBAC concentration from 5-wt% (0.3 MPa, 277 K) to 15-wt% (0.25 MPa, 285 K). Moreover, an increase of 9 K in the reactor can be achieved, keeping the mole fraction relatively constant, by increasing the TBAC concentration from 5-wt% (0.86 MPa, χ_{CO2} 9.1x10⁻³ at 279 K) to 15-wt% (1.37 MPa, χ_{CO2} 9.5x10⁻³ at 288 K).

Results of both methane and carbon dioxide systems show that solubility increases while increasing pressure. However, solubility is not a strong function of pressure but temperature and TBAC concentration. Hence, a higher temperature can be reached in the reactor as the TBAC concentration increases keeping the pressure and mole fraction relatively constant.

6. Bibliography

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