The effects of Tetra-n-butyl ammonium bromide and Tetra-n-butyl ammonium chloride on the phase equilibria, solubility and modelling of propane hydrate formation.

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Abstract

Gas hydrates are the largest known source of natural gas. They not only present a vast source of future energy but can further be used in renewable technology towards carbon capture. Unfortunately, while their existence presents an unlimited array of opportunities for the future, it provides deadly disasters at the present. The deep-water horizon oil spill that killed 11 oil operators and cost 62 billion dollars was caused by gas hydrates. Gas hydrates form at high pressure and low temperatures, and a strong understanding in their thermodynamics is required to not only tap their future potential but to prevent present disasters. This study focuses on the thermodynamics of propane hydrates. It is the first study to provide experimental thermodynamic phase equilibrium diagrams, solubility data and phase equilibria models for pure propane clathrates, and systems holding thermodynamic promoters under hydrate-liquid-vapor equilibrium conditions. Thermodynamic promoters help form semi-clathrates at higher temperature and lower pressures; however, this study is the first to provide strong evidence of the apposite under extremely low concentrations. Both tetra-n-butylammonium chloride (TBAC) and tetra-n-butyl ammonium bromide (TBAB) were used as salt additives to liquid water as thermodynamic promoters. The major issue with investigating propane hydrates is that pure propane holds a low vapor liquid equilibrium, and liquifies before

reaching the reactor at the pressures theoretically required for hydrate formation at temperatures above 5 °C. Furthermore ice can form at temperatures below 0 °C. This results in a low range of temperatures that can be used for hydrate formation under very low driving pressures above equilibrium. To make it harder, the thermodynamic dissociation of pure TBAC and water crystals at concentrations of 10.4 wt % TBAC under ambient conditions is reported in this study to be 6.67 °C. This means that gas hydrates would not form at this concentration, and lower concentrations were used until hydrate formation was found at 2.1 wt % TBAC. Mixtures holding the same concentration of TBAB and TBAC were used because of similar dissociation temperatures for both thermodynamic promoters with water. Ultimately, the study concludes that at these low concentrations, both salts inhibit hydrate formation leading to propane liquid water salt semi-clathrate formation at lower temperatures and higher pressures. The study further reports that the inhibiting effect increases with lower concentrations of the salt.

Abstrait

Les hydrates de gaz sont la source d'énergie la plus large parmi les sources connues de gaz naturel. Ils représentent une vaste source d'énergie disponible pour le futur. Malheureusement, malgré la multitude de possibilités d'exploitation que les hydrates de gaz offrent dans le futur, leur existence a eu des effets dévastateurs récemment. Le déversement de pétrole dans le golf du Mexique qui a entrainé la mort de 11 opérateurs pétroliers et a couté 62 milliards de dollars fut causé par les hydrates de gaz. Les hydrates de gaz sont formés en présence de hautes pressions et compréhension températures basses. Une robuste des mécanismes thermodynamiques est nécessaire pour accéder à leur futur potentiel ainsi que pour prévenir des désastres en temps présents. Cette étude est donc centrée sur les principes thermodynamique des hydrates de propane. C'est la première étude qui fournit des diagrammes expérimentaux de phases thermodynamiques, des données de solubilité, des modèles d'équilibre de phase des clathrates de propane pur, et des systèmes qui maintiennent les promoteurs thermodynamiques sous des conditions d'équilibre entre l'hydrate, l'eau et la vapeur. Les promoteurs thermodynamiques facilitent la création de semi-clathrates à des températures plus élevées et pressions plus basses que ce qui serait requis en leur absence, mais cette étude est la première à fournir une évidence solide de l'effet inverse en présence de concentrations extrêmement faibles. Le chloride de tétra-n-butylammonium (TBAC) et tétra-n-

butyl ammonium bromide (TBAB) furent utilises comme additifs de sel à l'eau liquide en tant que promoteurs thermodynamiques. La plus grande complication qui soit intervenue lors de l'étude des hydrates de propane est que le propane pur a un équilibre liquide-vapeur bas, et se liquéfie avant d'atteindre le réacteur aux températures prédites par la théorie, c'est-à-dire au-dessus de 5 °C. De plus, la glace se formant dès que la température dépasse 0 °C, le nombre de températures qui peuvent être utilisées pour former des hydrates sous des pressions au-dessus de l'équilibre liquide-vapeur est limitée. De plus, la dissociation thermodynamique de TBAC pur et de cristaux d'eau aux concentrations de 10.4% TBAC aux conditions ambiantes est présenté dans cette étude comme étant 6.67 °C. En d'autres termes, les hydrates de gaz ne se formant pas à cette concentration, de plus basses concentrations furent utilisées jusqu'à ce que la formation d'hydrates soit trouvée, à 2.1 wt % TBAC. Les mélanges qui contenaient la même concentration de TBAB et TBAC furent utilisées puisqu'elles ont des dissociations similaires en termes de température pour les promoteurs thermodynamiques ainsi que l'eau. Cette étude conclut qu'étant présents en concentration si basse, les deux sels inhibent la formation d'hydrates qui mènent à la formation du système d'équilibre de propane, eau liquide, sel et semi-clathrate avec des températures plutôt basses et pressions plus élevées. De plus, cette étude trouve que l'effet inhibiteur augmente plus la concentration de sel diminue lorsque la concentration est faible.

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Table of Contents

1. Introduction	. 1
2. Background	.5
2.1 Historical Perspective	.5
2.2 Gas Hydrates	.6
2.3 Phase equilibria	.8
2.4 Semi-Clathrates and Thermodynamic Promoters	.9
3. Experimental Procedure	11
3.1 Experimental Setup	11
3.2 Materials	11
3.3 Procedure for Equilibrium Experiments	12
4. Mathematical Procedure for Vapor-Liquid water-Hydrate Equilibrium Model	15
5. Results and Discussion	21
5.1 Phase Equilibrium Experimental Measurements	21
5.2 Phase Equilibrium Models	25
5.3 Solubility Calculations and Results	29
6. Conclusion	36

Figures

Figure 14: The solubility of propane in the liquid phase at equilibrium points for Liquid water, hydrate,	
propane with 1.49 wt % TBAC	5

Tables

Table 1:Critical parameters of different compounds for the Trebble-Bishnoi equation of state (23)10	б
Table 2:Interaction parameters between water-gas for the Trebble-Bishnoi equation of state (26)10	б
Table 3:Amj and Bmj values for the hydrate cage (27)1	7
Table 4:Physical and thermodynamic values for the hydrate cage (30)19	9
Table 5: Fitted Constant for Thermodynamic Phase Equilibria Modelling	б
Table 6: Calculating the AARE for different systems holding propane liquid water hydrates	9
Table 7: Solubility data for phase equilibria points of the system (Propane-liquid water-vapor- hydrates)	
	2
Table 8: Solubility data for phase equilibria points of the system (Propane-liquid water-vapor-hydrates)	
with 2.1 wt % TBAB	2
Table 9: Solubility data for phase equilibria points of the system (Propane-liquid water-vapor-hydrates)	
with 1.49 wt % TBAC	2

1. Introduction

Gas hydrates are crystalline molecules composed of a lattice most often made of ice in nature that surrounds a single molecule that interacts with other molecules in a gaseous manner at ambient conditions (1). When the lattice is made up of water, which is held together through hydrogen bonding, the gas hydrate is called a clathrate (1). While these hydrates present a large source of untapped future energy where there is over 10^{16} kg of carbon trapped in oceanic sediments, it presents a large source of danger in the oil industry through pipe plugging (2). The main application of this study is to better understand how propane interacts with water and thermodynamic promoters towards forming hydrates so that engineers can better predict when liquified petroleum gases that are mainly made of propane and butane will form hydrates under humidity during storage and transportation (3). This study also provides thermodynamic phase equilibria solubility information and phase compositions that are crucial towards the development of kinetic models for future propane hydrate reactor design (4).

Both Tetra-n-butylammonium chloride (TBAC) and Tetra-n-butylammonium bromide (TBAB) are thermodynamic promoters that interact and take part with the water lattice normally found with clathrates to make hydrate formation more energy favorable (5). At a thermodynamic level, this means that semi-clathrates, which are hydrates made up of promoters that take part of the lattice, are supposed to form at higher temperatures and lower pressures than they would without the promoter (6). The concentration of the promoter influences its effect on the thermodynamics of hydrates formation often having a peak concentration that leads to the most energy favorable hydrate formation (7).

Propane has a low vapor liquid equilibrium compared to other commonly used gases in industry such as methane and carbon dioxide (8) (9). This makes experiments difficult as propane can liquify under relatively low pressures as it moves from room temperature to a cold temperature-controlled reactor, and in turn prevents hydration formation. This can further lead to misleading results since the cloudy appearance of hydrates within water is similar to the appearance of liquified propane within water. The vapor liquid equilibrium of pure propane is below the equilibrium curve for liquid water propane hydrates at temperatures above 5 °C, indicating that propane hydrates cannot form at temperatures above this. Further, the possibility of water nucleating to ice before hydrate formation is possible below 0 °C, and as a result of this, temperatures only between the two can be used to study the equilibrium of liquid water propane hydrates. The following figure was developed using Antoine's Equation for the liquid vapor equilibrium of propane and literature results for propane liquid water hydrates to illustrate the existing temperature restriction when studying the given system (10).



Figure 1: Propane Vapor Liquid Equilibrium and Propane Liquid Water Hydrate Curve

As shown in the figure, propane hydrate formation is extremely difficult at higher temperature because not only is there a lower driving force for nucleation in terms of temperature, but there's much less available driving force in terms of pressure between the vapor liquid equilibrium of propane and the propane liquid water hydrate equilibrium curve. At a very high level, the presented figure displays that hydrate formation is impossible below the exponential curve, that it is possible in between the exponential and linear curve, where the higher the pressure the more probable, and is again impossible above or on the linear curve due to the formation of liquid propane. Once propane hydrates form for a given driving pressure, the pressure will decrease in a linear manner with time and eventually reach and stabilize at the equilibrium pressure shown near the exponential curve. This means that if after a 90-hour period, if the pressure doesn't start to decrease linearly, it is likely because the pressure selected for the experiment for a given temperature is below the propane liquid water hydrate equilibrium curve.

Equations of state were used to model the phase equilibria of pure propane liquid water hydrates and its formation under different concentrations of TBAB and TBAC. The gas and liquid fugacity was found using the Trebble-Bishnoi equation of state and the modified version of the van der Waals-Platteeuw model, and the Monte Carlo Optimization model was used to optimize theoretical parameters (11).

This study is the first to provide solubility and composition data of propane liquid water hydrates at the phase equilibrium condition, and is the first to investigates how thermodynamic promoters such as Tetra-n-butyl ammonium chloride and Tetra-n-butyl ammonium bromide influence the thermodynamics and solubility of these hydrates.

2. Background

2.1 Historical Perspective

The documented discovery of gas hydrates was in 1810 when Sir Humphrey Davy saw that chlorine gas dissolved in water would freeze at temperatures up to 9 °C (12). The phenomena gained the interest of chemists who later investigated the different chemicals and ratios where hydrates would form. It wasn't until 1934 that it gained the attention of chemical engineers when they were found blocking natural gas transmissions (13). Chemical engineers worked in the field of flow assurance for the petroleum industry, which primarily involved predicting and inhibiting hydrate formation (14). These predictions involved building phase equilibrium curves to correctly determine when hydrate nucleation was possible (14). In the 1960's, gas hydrates were found in Siberian permafrost (15). From there, the scientific community paid close attention at marine sediments and gas hydrates to conclude that it is the largest known source of energy on this planet (15). Currently, significant research is being done on using gas hydrate pellets for transportation and storage of natural gases from off shore oil sites to land through boats, as well as for carbon sequestration (16). Unfortunately, these studies are still mostly done at small scales, and are not realistically going to be applied soon without larger scale studies. With the highly popularized recent BP oil spill accident caused by hydrate

formation, the dangers of hydrates have been reintroduced to the general population (17). The research presented in this work, while at a small scale, applies to all situations towards the hydrate prediction, as its focus is on its thermodynamics instead of kinetics (18).

2.2 Gas Hydrates

Gas hydrates hold a host molecule that forms a crystal lattice surrounding a single molecule often found in the gas phase under ambient conditions (19). The crystal lattice can be made of different chemicals such as ammonia but is mostly found as water in nature. These gas hydrates with a lattice made of water molecules are called clathrates. The crystal lattice in a clathrate is held together by hydrogen bonds and by weak Van der Waals forces between the guest molecule and the lattice. The guest molecule holds a radius smaller than the cavity of the crystal lattice cage and cannot interfere with the hydrogen bonding in the lattice for the cage to be thermodynamically stable (19).

The following figure describes the three most common types of hydrates, structure 1 (SI), structure 2 (SII) and structure H (SH) (20). SI hydrates are the most

common and hold the smallest cavity volume, holding 12 pentagonal faces and 2 hexanol faces. 6 of them combine together that uses a unit cell structure that uses 46 water molecules in total (20). SII structures are less common and larger, holding 12 pentagonal faces and 4 hexagonal faces (20). 8 of them combine together to form unit cell structures that use 136 water molecules in total (20). The research done in this work on propane is on SII hydrates (20). The last known form of hydrates, structure H, holds 12 pentagonal faces and 8 hexagonal faces to form unit cell structures that use 34 water molecules in total (20).



What Are Gas Hydrates?

Figure 2: Gas Hydrate Structures (20)

2.3 Phase equilibria

Understanding the thermodynamic phase equilibrium of gas hydrates is crucial in identifying the pressure and temperature conditions where hydrates will form and dissociate in the oil industry. From phase equilibria, mole fractions of different components of each phase is also obtained. In nature, hydrate equilibrium is most often three phases holding vapor liquid and gas hydrate solids co-existing together; however, other phases can exist such as ice.

As shown in the figure below, the thermodynamic phase equilibrium curve describes the temperatures and pressures for hydrate formation. Above and on the curve, hydrates can exist and will eventually form (21). Below the curve, hydrates will never exist (21). Once hydrate nucleation occurs in a temperature controlled environment, the pressure will decrease in a linear manner with time until it stabilizes at the equilibrium pressure for hydrate formation (21). Unless hydrates are already present, where hydrate dissociation would increase reactor pressure, the pressure within a reactor will not change below the phase equilibria curve (21).



*Figure 3: Thermodynamic Phase Equilibria of Gas Hydrates in Deep Water (21)***2.4 Semi-Clathrates and Thermodynamic Promoters**

A semi-clathrate is a gas hydrate that has a crystal lattice made up of water molecules and other compounds such as salts. These salts include thermodynamic promoters such as TBAC and TBAB. Normally these salts make semi-clathrate formation more thermodynamically favorable over normal hydrates where they can nucleate at higher temperatures and lower pressures; however, the findings in this work show different at very low concentrations (22). At normal concentrations, the tetra-n-butylammonium cations (TBA+) and the guest molecule are located in the center of the tetragonal cages while the halide (Cl- and Br- respectively) are integrated within the lattice by hydrogen bonds (22). Unlike normal gas hydrates that require a guest molecule normally in the gas phase at ambient conditions within the cage to stabilize the structure with weak Van der Waal forces, semi clathrates can form at without a "gas" guest molecule due to the cation found within the cage stabilizing the structure (22). This additional stability is what theoretically makes semi-clathrate formations more thermodynamically favorable (22). The semi-clathrate structure holding the anion and cation parts of TBAB is shown in the following figure.



Figure 4: TBAB and Water Semi-Clathrate Structure (22)

3. Experimental Procedure

3.1 Experimental Setup

The experimental setup consists of a 600 cm³ stainless steel reactor (SS360) with a mounted stirrer, a viewing window and a port at the bottom of the reactor to collect hydrate samples once an experiment is complete. A glycol water bath is used to control reactor temperature, a Rosemount transducer was used to measure pressure (span of 0-14 MPa and an accuracy of $\pm 0.065\%$), and an Omega platinum resistance temperature device probe was used to measure liquid and gas temperature in the reactor.

3.2 Materials

Ultra-high purity propane gas (99.99%) was obtained from MEGS Inc, and both A 50 weight percent (wt%) aqueous solution of Tetra-n-butylammounium bromide (TBAB), as well as a pure salt container of Tetra-n-butylammonium chloride (TBAC) was purchased from Sigma Aldrich.

3.3 Procedure for Equilibrium Experiments

First, 1 L aqueous solution of the desired solution of aqueous TBAB, TBAC, TBAB+TBAC or pure reverse osmosis water was made. A refractometer was then used to confirm the estimated concentration. 360 mL of the studied solution was used to wash the reactor three times where the reactor held a holdup volume of 400 mL. Afterwards, 360 mL of the studied solution was placed inside the reactor. A space of 40 mL was left so that the experimenter could detect the formation of liquid propane due to too high reactor pressures by the change in liquid height from the viewing port.

The temperature within the reactor was placed near 5 °C. The reactor pressure was then placed to 450 kPa absolute and then depressurized to 150 kPa. This process was repeated three times to ensure air was not present within the reactor. The reactor was then brought below the vapor liquid equilibrium line, substantially above the theoretical propane liquid water hydrate phase equilibrium point to ensure that sufficient driving force was present to drive hydrate nucleation. Even with the highest possible driving forces, nucleation followed by the decrease in pressure with time to phase equilibrium would take in between 12 to 96 hours. Phase equilibrium was said to be achieved when the pressure changed less than 1 kPa within an hour of measurement.

Once phase equilibrium was found, the temperature and pressure were recorded, and a 10 mL sample bomb was placed at the bottom port of the reactor. The experiments were later repeated with another sample bomb. This had to be done instead of using a 20 nm nominal rating often used for other experiments in this laboratory to take 5 samples at a time because of the low pressures found in the reactor that would not fill the apparatus at necessary levels for the study. Prior to attaching the sample bomb, they were weighted, vacuum pumped and chilled to ensure thermal consistency. Liquid was further removed from the bottom reactor port before placing the sample bomb. Once a sample was taken, it was placed in a gasometer where the sample bombs were left to depressurize. After an hour, the volume of gas, air temperature, and atmospheric pressure were tank. The sample bomb weight was then retaken, and the concentration of the solution was then remeasured with a refractometer. The sample bombs were then washed with reversed osmosis water, and the process was repeated for another fixed temperature. The following diagram describes the calculations later taken for each step of the research experiment.



Figure 5:Experimental Setup and Procedure for Solubility data taken from Gasometer

4. Mathematical Procedure for Vapor-Liquid water-Hydrate Equilibrium Model

The following steps were used to model the vapour-liquid water-hydrate phase equilibrium of the following fours systems:

- Propane+Water
- Propane+Water+ TBAC
- Propane+Water+ TBAB
- Propane+Water+ TBAC+ TBAB

First, at phase equilibrium, the fugacity of each component is equal for every phase as shown below

$$f_i^H(T, P) = f_i^L(T, P) = f_i^V(T, P)$$
 $[i = 1, ..., N]$ Equation 1

where N is the total number of components in the system and f_i^{π} is the fugacity of component *i* in phase π .

Second, the Trebble-Bishnoi equation of state was used to calculate the fugacity of each component in the liquid and vapor phase. It was assumed that no salts were found in the gas phase because of their non-volatile nature. It was further assumed that the salts did not change the solubilities of the gas in the liquid phase (23) (24). The critical properties used in the equation of state are shown in Table 1. Table 2 shows the interaction parameters between water and propane which were calculated by using a Newton-Raphson optimization methodology, as well as using propane liquid-vapor equilibrium data provided from Gaudette (25).

Table 1:Critical parameters of different compounds for the Trebble-Bishnoiequation of state (23)

Compone	_ (=)	P _c		d _c			
nt	$T_{c}(K)$	(MPa)	ω	(m ³ /mol)	ζc	q_1	q ₂
					0.2440		
H ₂ O	647.286	22.09	0.34375	18.03	0.2110	0.46195	0.23002
					3		
C U	2.000	4 075	0 1 5 1 5		0.2993	0 48586	0.1.6600
C_3H_8	369.85	4.275	0.1515	60.7	9	0.47576	0.16608

Table 2:Interaction parameters between water-gas for the Trebble-Bishnoiequation of state (26)

Components	K _A	K _B	K _C	K _D
C ₃ H ₈ -H ₂ O	0	0.1	0.57	0.47

Third, Van der Waals and Platteeuw model was used to calculate the chemical potential of water in the hydrate phase where f_j is the fugacity of the hydrate former j, not including water in the hydrate phase. (27):

$$-\frac{\Delta\mu_w^{\beta-H}(T,P)}{RT} = \sum_{i=1}^{NS} \ln\left(1 + \sum_{j=1}^{NH} C_{i,j}(T)f_j(T,P)\right)^{-\nu_i}$$
 Equation 2

The correlation proposed by Parrish and Prausnitz was then used to calculate the Langmuir constant (C_{mj}) (28). The parameters used within this equation are fitted constants about the hydrate cage and are shown in the following table.

$$C_{mj} = \frac{A_{mj}}{T} \exp\left(\frac{B_{mj}}{T}\right)$$
 Equation 3

	Small	Cage	Large	Cage
Component	$\mathbf{P} \times 10^{-3}$			$B \times 10^{-3}$
Component	$A_{mj} \times 10^{3}$ (K bar ⁻¹)	(K)	$\begin{array}{c} A_{mj} \times 10^3 \\ (K \text{ bar}^{-1}) \end{array}$	(K)
C ₃ H ₈	0	0	10.24	4.560

Table 3: Amj and Bmj values for the hydrate cage (27)

Fourth, the equations presented in step 3 are rearranged where the fractional occupancy is represented by v_m .

$$\frac{\Delta V_w^{MT-L_v}}{RT_f} - RT_f \sum_{m=1} v_m \ln\left(1 + \sum_{j=1}^{NH} C_{mj}\hat{\phi}_j y_j P\right) + \Psi(T) = 0$$

$$= g(P)$$
Equation 4

Where

$$\Psi(T) = \frac{\Delta \mu_w^o}{RT^o} + \frac{\beta}{2R} (T_0 - T) + \frac{\Delta C_p - \beta T^o}{R} \ln\left(\frac{T_o}{T}\right)$$

$$+ \frac{\Delta h_w^o - \Delta C_p^o T^o + \frac{\beta}{2} (T^o)^2}{R} \left(-\frac{1}{T_o} + \frac{1}{T}\right)$$
Equation

The parameters presented in the equation are thermodynamic constants based on the properties of the hydrate cage and hold the following values for structure 2 (29):

Table 4:Physica	l and thermo	odynamic val	lues for the	hydrate	cage (30))
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Property	Structure II
β	0.141kJ kmol ⁻¹ K ⁻²
ΔC_p^o	-38.13k J kmol ⁻¹ K ⁻¹
Δh_w^o	-5203.5kJ kmol ⁻¹
$\Delta \mu_w^o$	883kJ kmol ⁻¹
$\Delta V_w^{MT-L^o}$	0.005m ³ kmol ⁻¹
<i>v</i> ₁	2/17
v_2	1/17
T ^o	273.15K

When salts were considered in the model (TBAB/TBAC), an adjustment factor was added to the values of A_{mj} and B_{mj} and the occupancy parameters v_1 and v_2 were also changed to reflect a change in gas particle occupancy as shown by the following equations where c, d, e and f are adjustment parameters:

$$A_{mj}^* = cA_{mj}$$

 $B_{mj}^* = dB_{mj}$
 $v_1^* = ev_1$

The adjustment parameter were found using the Monte-Carlo optimization method. With these parameters, the temperature and pressure for vapor liquid hydrate phase equilibria of different propane liquid water salt systems were obtained.

 $v_2^* = fv_2$

5. Results and Discussion

5.1 Phase Equilibrium Experimental Measurements

I started performing experiments to examine how TBAC influences the thermodynamic phase equilibria of propane liquid water hydrate systems. After performing experiments at a system concentration of 10.4 wt % TBAC, I concluded that gas hydrates were impossible to form at this concentration. Morphologically, hydrates were forming with cloudy formations being visible from the view port; however, these were empty hydrates. I then found through literature search that the thermodynamic dissociation equilibrium temperature for 10 % wt TBAC + Liquid Water Hydrates is at 6.4 °C, and that hydrates holding propane molecules within them were impossible to form below this temperature for an aqueous solution hold 10 % wt TBAC (31). This presented a major problem, since theoretically pure propane liquid water hydrates can only form at temperature below this between 0 °C to 5 °C since its phase equilibria curve is above the vapor liquid equilibrium of propane gas above this range. I then worked on determining the thermodynamic dissociation equilibrium temperature for 10.4 wt% TBAC + Liquid Water Hydrates and found it to be at 6.67 °C. The thermodynamic dissociation equilibrium temperature between TBAC and Water for a concentrations of 5 % wt TBAC and 10 % wt TBAC is 2.3 °C and 6.4 °C respectively (31). Using linear extrapolation, a concentration of 2.1 wt % TBAC was selected as it holds a theoretical thermodynamic dissociation temperature of -0.078 °C. I then ran experiments using this concentration and a lower concentration of 1.49 wt % TBAC. Overall 9 different thermodynamic phase equilibrium were found for the system at 2.1 wt % TBAC and 5 for 1.49 wt % TBAC. The results provided equilibrium pressures that were slightly higher than the equilibrium pressure without the salt. This was highly unexcepted as the salts were supposed to facilitate hydrate formation and instead inhibited it.

I wanted to verify the experimental results for the propane liquid water hydrate system with TBAC by performing experiments on a pure propane liquid hydrate system. The idea was that if the phase equilibrium curves built during the experiments followed the existing phase equilibrium curves for the same system in literature, then the results found with the addition of TBAC would be more justifiable. I found that no existing sources in literature provided solubility data for pure liquid water propane hydrate system, and decided to further perform solubility experiments for this system at equilibrium to provide novel results. Overall, the phase equilibrium curve that I built was almost identical to literature at points within the 2 °C to 3 °C overlap between the experiments and literature search is presented in the following figure.



Figure 6:Thermodynamic Phase Equilibrium of Propane Liquid Water Vapor Hydrates Through Experimentation and Through Literature Search

The following figure provides the experimental results for two concentrations of TBAC and the experimental results for the propane liquid water hydrate baseline phase equilibria curve built with the same reactor setup. Curve fits were shown on the experimental data to help visualize the effects of the salt at different concentrations. From the results, it can be concluded that TBAC acts as an inhibitor at low concentration along the range of 2 wt% and that at higher weight percentages

of TBAC at these low percentages, the inhibition caused by the salt becomes stronger.



Figure 7: Phase Equilibria of Propane Liquid Water Vapor Hydrates with various concentrations of TBAC

Another thermodynamic phase equilibrium curve was built for 2.1 wt % TBAB. This concentration was chosen because TBAB holds a thermodynamic dissociation temperature for its empty hydrates that is on average less than 0.5 °C

different than the empty hydrate cages formed by TBAC and water (31). The inhibitory effects of the salt at low concentration was also found for TBAB towards hydrate formation, where it was found to hold a lower influence on thermodynamic phase equilibrium than TBAC.



Figure 8: Phase Equilibria of Propane Liquid Water Vapor Hydrates with 2.1 % wt TBAB

5.2 Phase Equilibrium Models

The following tables describe the fitted constants found through the modelling the various propane liquid water hydrate equilibrium curves with different salts. Fitted constants are not shown for the hydrate equilibrium curve found without salts because were not required for the model. The fitted constants are defined in Equation 6 in section 4.

Constant	2.1wt% TBAB	2.1wt% TBAC	1.49wt% TBAC
С	1.669	1.6982	1.3755
d	1.771	1.9984	1.6027
е	1.6495	0.1000	1.2960
f	0.7361	0.5418	0.7030

Table 5: Fitted Constant for Thermodynamic Phase Equilibria Modelling

The following page holds an array of figures, comparing the thermodynamic phase equilibrium points found through the model to the experimental values. The curves shown demonstrate the exponential fit for the models. The models provided theoretical equilibrium pressures for equilibrium temperatures controlled during the experiments.



Figure 9: Thermodynamic Phase Equilibrium Model for Propane Liquid Water Vapor Hydrates



Figure 10: Thermodynamic Phase Equilibrium Model for Propane Liquid Water Hydrates with TBAB



Figure 11: Thermodynamic Phase Equilibrium Model for Propane Liquid Water Vapor Hydrates with TBAC

The Average Absolute Relative Error (AARE) is used as a measure of model fit with the experimental data and is shown for a general variable *y* in the following equation.

$$\% AARE = \frac{100}{n_{data}} \sum_{k=1}^{n_{data}} \left| \frac{y_k^{exp} - y_k^{model}}{y_k^{exp}} \right|$$
Equation
7

The table below shows the % AARE values found for all models. As expected, the baseline thermodynamic phase equilibrium curve for propane liquid water hydrates held the least error as it did not require fitted parameters. Surprisingly, the modelling strategy was found to work better with the salt TBAC than TBAB.

 Table 6: Calculating the AARE for different systems holding propane liquid water

 hydrates

	2.1wt% TBAB	2.1wt% TBAC	1.49wt% TBAC	Baseline
AARE (%)	23.2	9.8	10.2	3.2

5.3 Solubility Calculations and Results

Solubility was calculated following several calculations after running experiments with the gasometer. First, the assumption that the gas recovered within the gasometer was only made up of water vapor and propane was made. The mass of each chemical in the gas phases was then found under ambient conditions under the ideal gas law.

$$m_i^V = \frac{P_i V_{gasometer} M w_i}{RT_{ambient}}$$

Equation 8

Using Antoine's equation to calculate water pressure at ambient temperature, the guess gas pressure was found through subtracting the total pressure to the theoretical water pressure (32).

The weight of the liquid after depressurization cam then be found using the following:

$$m_o^L = m_o - m_g^V - m_w^V$$
 Equation 9

If a salt was found in the solution, its weight fraction was computed using a refractometer. The salt and water mass in the liquid was then found using the following:

$$m_t^L = m_o^L * x_t$$
 Equation 10

$$m_w^L = m_o^L * (1 - x_t)$$
Equation 11

With Henry constants found in the NIST webbook, the fraction of guest gas remaining in the liquid was found (9). This value was less than 0.1 % of the moles of liquid water. Because of this it was not considered in calculating the number of moles of liquid water. Standard deviation for mole fractions was then found, where y is a general variable, \bar{y} is the average of a given set of n values of y, and s is the standard deviation (33) :

$$s = \sqrt{\frac{\sum_{k=1}^{n} (y_k - \bar{y})}{(n-1)}}$$
 Equation 12

Uncertainty is then found using the following equation. The length of the error bars in the solubility data points represent the uncertainty multiplied by a factor of 2:

$$u = s/\sqrt{n}$$
 Equation 13

The following tables summarize the solubility results found for all propane liquid water hydrate systems studied at phase equilibria where solubility experiments were successful. Unsuccessful runs were the result of either a hydrate clogs within the reactor blocking liquid flow due to a large formation period and little gas pressure, gas leaks at the liquid port, or gas leaks between the sample bombs and gasometer.

T/°C	Pabs/kPa	xC3H8	s(xC3H8)	u(xC3H8)
2.61	301	8.66E-4	1.72 E-4	1.21 E -4
1.85	266	4.71 E-4	1.5 E-5	1.08 E -5
0.14	178	2.27 E-4	1.9 E-5	1.35 E -5

Table 7: Solubility data for phase equilibria points of the system (Propane-liquid
water-vapor- hydrates)

Table 8: Solubility data for phase equilibria points of the system (Propane-liquid
water-vapor-hydrates) with 2.1 wt % TBAB

T/°C	Pabs/kPa	xC3H8	s(xC3H8)	xTBAB	s(xTBAB)	u(xTBAB)
2.58	315	5.03 E-4	0.33 E-4	125.469 E-5	0.0056 E-5	2.37 E -5
1.18	231	4.42 E-4	0.63 E-4	125.479 E-5	0.010 E-5	4.42 E -5
0.08	180	4.08 E-4	0.07 E-4	125.485 E-5	0.0012 E-5	0.527 E -5

Table 9: Solubility data for phase equilibria points of the system (Propane-liquidwater-vapor-hydrates) with 1.49 wt % TBAC

T/°C	Pabs/kPa	xC3H8	s(xC3H8)	xTBAC	s(xTBAC)	u(xTBAC)
2.56	322	4.83 E-4	0.848 E-4	97.886 E-5	0.0848 E-3	0.0599 E-3
1.91	264	4.3 E-4	0.041 E-4	97.893 E-5	0.0041 E-3	0.0229 E-3
0.32	191	3.36 E-4	0.005 E-4	97.905 E-5	0.0005 E-3	0.00037 E-3
1.07	229	3.73 E-4	0.13 E-4	97.901 E-5	0.0130 E-3	0.0092 E-3

The following figures summarizes the solubility trends found for each system. For 1.49 wt % TBAC and 2.1 wt % TBAB the results showed that solubility increases in either an exponential manner with a small second rate of change or a linear manner. For pure propane liquid water hydrates, the solubility was found to be exponential with a high second rate of change. The error bars are represented by the standard error.



Figure 12: The solubility of propane in the liquid phase at equilibrium points for propane liquid water vapor hydrates



Figure 13: The solubility of propane in the liquid phase at equilibrium points for Liquid water, hydrate, propane with 2.1 wt % TBAB



Figure 14: The solubility of propane in the liquid phase at equilibrium points for Liquid water, hydrate, propane with 1.49 wt % TBAC

6. Conclusion

This study is the first to the experimenters' knowledge to provide strong evidence of a thermodynamic promoter inhibiting hydrate formation under extremely low concentrations. The major issue with investigating propane hydrates is that pure propane holds a low vapor liquid equilibrium, and that low driving forces for hydrate nucleation leads to long experiments that are hard to repeat. Prior to lowering to concentration of TBAC to a level where propane liquid water vapor hydrates could form, it was found that TBAC and liquid water starts to form hydrates on its own without gases at 6.67 °C for aqueous solutions holding 10.4 wt % TBAC. This study also reports that hydrate formation holding propane was found at 2.1 wt % TBAC. TBAC was found to hold a stronger inhibitory effect towards hydrate formation than TBAB; however, when both salts were mixed together, evidence shows that their individual inhibitory effects are antagonistic. Ultimately, this study provides novel insights on propane liquid water hydrates with both solubility data that was not previously available for the pure three phase system, and with phase equilibria, modelling, and solubility data for the system with TBAB and TBAC.

List of Symbols

f

g

γ

ν

ρ

S

Х

AARE average absolute relative error

- Langmuir constant (Pa⁻¹) С fugacity (Pa) objective function activity coefficient chemical potential (J/mol) μ Ν hydration number Avogadro's number N_A number of cavities per water molecule pressure (Pa) Р universal gas constant (J/mol K) R density (mol/m³) standard deviation temperature (K) Т molar volume (m³/mol) V mole fraction
- general variable у

Subscripts

- j component j
- cage type i i
- W water

Superscripts

- H hydrate
- L liquid
- V vapour
- β empty clathrate
- π phase pi
- sat saturation

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- 1. Vaidya S. Clathrates An exploration of the chemistry of caged compounds. Resonance. 2004 Jul;9(7):18–31.
- 2. Buffett BA. Clathrate Hydrates. [cited 2018 Sep 8]. Available from: https://pdfs.semanticscholar.org/3300/ac8dc4d8352358a597b90d6397527a124 dd2.pdf
- Giavarini C, Maccioni F, Santarelli M. Formation Kinetics of Propane Hydrates - Industrial & Engineering Chemistry Research (ACS Publications) [Internet]. [cited 2018 Sep 8]. Available from: https://pubs.acs.org/doi/abs/10.1021/ie0207764
- 4. Bergeron S, Servio P. CO2 and CH4 mole fraction measurements during hydrate growth in a semi-batch stirred tank reactor and its significance to kinetic modeling. Fluid Phase Equilibria. 2009 Feb 25;276(2):150–5.
- Eslamimanesh A . Application of gas hydrate formation in separation processes: A review of experimental studies - ScienceDirect [Internet]. [cited 2018 Sep 8]. Available from: https://www.sciencedirect.com/science/article/pii/S0021961411003570
- Zhong D. Influence of Cyclopentane and SDS on Methane Separation from Coal Mine Gas by Hydrate Crystallization - Energy & Fuels (ACS Publications) [Internet]. [cited 2018 Sep 8]. Available from: https://pubs.acs.org/doi/10.1021/ef401491e
- Kobori T, Muromachi S, Ohmura R. Phase Equilibrium for Ionic Semiclathrate Hydrates Formed in the System of Water + Tetra-nbutylammonium Bromide Pressurized with Carbon Dioxide. J Chem Eng Data. 2015 Feb 12;60(2):299–303.
- Kumar R . Structure and kinetics of gas hydrates from methane/ethane/propane mixtures relevant to the design of natural gas hydrate storage and transport facilities - 2008 - AIChE Journal - Wiley Online Library [Internet]. [cited 2018 Sep 8]. Available from: https://onlinelibrary.wiley.com/doi/abs/10.1002/aic.11527

- 9. Propane [Internet]. [cited 2018 Sep 8]. Available from: https://webbook.nist.gov/cgi/cbook.cgi?ID=C74986&Mask=4
- 10. Sloan D. Clathrate Hydrates of Natural Gases, Second Edition, Revised and Expanded. CRC Press; 1998. 734 p.
- 11. Eslamimanesh A, Mohammadi AH, Richon D. Thermodynamic modeling of phase equilibria of semi-clathrate hydrates of CO2, CH4, or N2+tetra-n-butylammonium bromide aqueous solution. Chemical Engineering Science. 2012 Oct 22;81:319–28.
- 12. A Brief History of Methane Hydrate | HowStuffWorks [Internet]. [cited 2018 Sep 24]. Available from: https://science.howstuffworks.com/environmental/green-tech/energyproduction/frozen-fuel2.htm
- Hammershchmidt E. Formation of Gas Hydrates in Natural Gas Transmission Lines - Industrial & Engineering Chemistry (ACS Publications) [Internet].
 [cited 2018 Sep 24]. Available from: https://pubs.acs.org/doi/abs/10.1021/ie50296a010
- 14. Wang Z, Zhao Y, Zhang J, Pan S, Yu J, Sun B. Flow assurance during deepwater gas well testing: Hydrate blockage prediction and prevention. Journal of Petroleum Science and Engineering. 2018 Apr 1;163:211–6.
- 15. Safronov AF, Shits EY, Grigor'ev MN, Semenov ME. Formation of gas hydrate deposits in the Siberian Arctic shelf. Russian Geology and Geophysics. 2010 Jan 1;51(1):83–7.
- 16. Mimachi H, Takeya S, Yoneyama A, Hyodo K, Takeda T, Gotoh Y, Natural gas storage and transportation within gas hydrate of smaller particle: Size dependence of self-preservation phenomenon of natural gas hydrate. Chemical Engineering Science. 2014 Oct 18;118:208–13.
- 17. BP's Deepwater Horizon costs total \$62B [Internet]. [cited 2018 Sep 25]. Available from: https://www.usatoday.com/story/money/2016/07/14/bp-deepwater-horizon-costs/87087056/
- Liu J-Y, Zhang J, Liu Y-L, Tan X-H, Zhang J. Experimental and Modeling Studies on the Prediction of Gas Hydrate Formation [Internet]. Journal of Chemistry. 2015 [cited 2018 Sep 25]. Available from: https://www.hindawi.com/journals/jchem/2015/198176/

- 19. Clathrate hydrates [Internet]. [cited 2018 Sep 25]. Available from: http://www1.lsbu.ac.uk/water/clathrate_hydrates.html
- 20. National Research Council. Charting the Future of Methane Hydrate Research in the United States, [Internet]. [cited 2018 Sep 25]. Available from: https://www.nap.edu/read/11094/chapter/4
- 21. Koh C. Towards a fundamental understanding of natural gas hydrates. Chem Soc Rev. 2002 May 7;31(3):157–67.
- 22. Eslamimanesh A, Mohammadi A, Richon D. The schematic picture of a typical semi-clathrate hydrate formed from a gaseous hydrate| Download Scientific Diagram [Internet]. [cited 2018 Sep 25]. Available from: https://www.researchgate.net/figure/The-schematic-picture-of-a-typical-semi-clathrate-hydrate-formed-from-a-gaseous-hydrate_fig1_256680412
- 23. Trebble MA, Bishnoi PR. Development of a new four-parameter cubic equation of state. Fluid Phase Equilibria. 1987 Sep 1;35(1):1–18.
- 24. Sun Z, Sun L. Phase equilibria, solubility and modeling study of CO2/CH4 + tetra-n-butylammonium bromide aqueous semi-clathrate systems
 - ScienceDirect [Internet]. [cited 2018 Sep 10]. Available from: https://www.sciencedirect.com/science/article/pii/S0378381214007389
- 25. Gaudette J. Phase equilibria and solubility measurements of gases in water in the hydrate formation region. 2007 [cited 2018 Sep 10]; Available from: http://digitool.library.mcgill.ca/R/?func=dbin-jump-full&object_id=18452&local_base=GEN01-MCG02
- 26. Trebble MA, Bishnoi PR. Extension of the Trebble-Bishnoi equation of state to fluid mixtures. Fluid Phase Equilibria. 1988 Oct 1;40(1):1–21.
- 27. Waals JHVD, Platteeuw JC. Validity of Clapeyron's Equation for Phase Equilibria involving Clathrates. Nature. 1959 Feb;183(4659):462.
- 28. Parrish WR, Prausnitz JM. Dissociation Pressures of Gas Hydrates Formed by Gas Mixtures. Ind Eng Chem Proc Des Dev. 1972 Jan 1;11(1):26–35.
- Klauda J, Sandler S. A Fugacity Model for Gas Hydrate Phase Equilibria -Industrial & Engineering Chemistry Research (ACS Publications) [Internet]. [cited 2018 Sep 10]. Available from: https://cdnpubs.acs.org/doi/10.1021/ie000322b

- 30. Holder G . Thermodynamic and Molecular Properties of Gas Hydrates from Mixtures Containing Methane, Argon, and Krypton - Industrial & Engineering Chemistry Fundamentals (ACS Publications) [Internet]. [cited 2018 Sep 10]. Available from: https://pubs.acs.org/doi/abs/10.1021/i160075a008
- 31. Sun Z . Phase Equilibrium and Latent Heat of Tetra-n-butylammonium Chloride Semi-Clathrate Hydrate [Internet]. [cited 2018 Sep 9]. Available from: https://pubs.acs.org/doi/pdf/10.1021/je2004116
- 32. Welcome to the NIST WebBook [Internet]. [cited 2018 Sep 9]. Available from: https://webbook.nist.gov/
- 33. Montgomery DC, Runger GC. Applied statistics and probability for engineers. 3rd ed. New York: Wiley; 2003. 706 p.