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EQUILIBRIUM DATA OF CO₂-BASED SEMI-CLATHRATES FROM QUATERNARY AMMONIUM SOLUTIONS

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ABSTRACT

CO₂ mitigation represents a major industrial and scientific challenge of this century, therefore CO₂ capture and sequestration is a route to solve a part of the problem, especially for the industries in which the gases to be treated are well localized. CO₂ capture by using hydrate formation has revealed to present an energetic interest because it is less intensive than other methods. In this process the cost of the separation is due to compression of gases to reach the gas hydrate formation conditions at which water and gas forms a solid that encapsulates preferentially CO₂. In fact, the hydrate formation requires high pressures and low temperatures, which explains the use of thermodynamic promoters to decrease the operative pressure. Quaternary ammoniums salts represent an interesting family of components because of their thermodynamic effect, but also because they can generate crystals that are easily handable. In this work, we have made experiments concerning the equilibrium of pure gas hydrates (CO₂, N₂ and CH₄) in presence of the tetra-*n*-butyl ammonium bromide (TBAB) and compared these data to literature. We have applied the Clausius-Clapeyron equation, to the results obtained and the literature data, thus observing that the hydrates have a pure component behavior. In the specific case of N₂-TBAB semi-clathrates, observations showed that the pressure is first order depending on the temperature only and independent from the TBAB concentration. For the CO₂-TBAB and CH₄-TBAB semi-clathrates the results are different. In fact, the equilibrium pressure is clearly dependent on both the temperature and TBAB concentration, for that reason the constant B from the Clausius-Clapeyron equation becomes a function of the TBAB concentration. Another point of our investigation is the effect of other types of quaternary ammoniums to find an additive that allows the formation of hydrates close to room temperature and atmospheric pressure.

Keywords: gas hydrate, quaternary ammoniums salts, CO₂, CH₄, N₂, phase equilibrium

NOMENCLATURE

A – Value used to relate $\ln P$ in function of $1/T$ for mixed hydrates [$\ln \text{MPa} \cdot \text{K}$]
B – Value used to relate $\ln P$ in function of $1/T$ for mixed hydrates [$\ln \text{MPa}$]
 ΔH – Heat of hydrate formation [$\text{J} \cdot \text{mol}^{-1}$]
 j – Type of cavity []
 m_j – Number of cavities with the type j []
P – Pressure [bar, MPa]
R – Perfect gas constant [$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$]
T – Temperature [K]
V – Volume [m^3]
 V_g – Gas specific volume [m^3]
 x_{TBAB} – Mass percentage of TBAB in solution [%]
z – Compressibility factor []

INTRODUCTION AND LITERATURE SURVEY

CO₂ is one of the most important greenhouse gases due to its global warming potential and long atmospheric residence time [1]. A great challenge is to reduce the CO₂ emissions by increasing the efficiency of the process and developing new technologies. The capture and sequestration is an interesting route to solve part of the problem. The capture of Carbon dioxide by gas hydrate formation is a new process for separating CO₂ from flue gases, by crystallizing liquid water with compressed flue gas to form a solid structure in which CO₂ is encapsulated preferentially. After precipitation, the hydrate slurry is dissociated and

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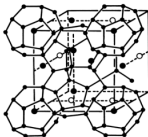
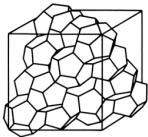
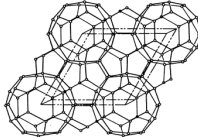
	SI		SII		SH		
							
Cavity	5^{12}	$5^{12}6^2$	5^{12}	$5^{12}6^4$	5^{12}	$4^35^66^3$	$5^{12}6^8$
Type of cavity (j : indexation number)	1	2	1	3	1	5	4
Number of cavity (m_j)	2	6	16	8	3	2	1
Average cavity radius (nm) (1)	0.395	0.433	0.391	0.473	0.391	0.406	0.571
Variation in radius,%(2)	3.4	14.4	5.5	1.73			

Table 1 - Structure of gas hydrates [3].

purified CO₂ is released at gas state and ready for sequestration. To decrease the formation pressure, additives from the quaternary ammonium family where the most commonly used is tetra-n-butyl ammonium bromide (TBAB) which also presents an interesting property to generate hydrate slurries that is naturally anti agglomerant [2].

Gas Hydrates

The clathrates are ice-like compounds; they correspond to a re-organization of the hydrogen links to form a solid in which the crystallographic structure is based on H-bonds links. The clathrates of water are also qualified improperly of “porous ice” because the crystal structure shows that the water molecules built a network of cavities in which could be captured gases, volatile liquids or other small molecules.

The clathrates hydrates, called gas hydrates, have been studied intensively in respect to their occurrence in deep sea pipelines where they cause hard problems of flow assurance. The gas hydrates can exhibit three different structures called SI, SII and SH [3] which are a combination of different types of polyhedral sharing faces between them. Jeffrey [4] suggested the nomenclature to describe each polyhedral: e is the number of edges of the face, and f is the number of faces with e edges. Currently, three different structures have been established precisely, called I, II and H (table 1).

Numerous hydrate formation data, for pure carbon dioxide and its binary mixtures in the presence of water, have been reported in the literature. Kang *et al* [5] presented data on the

three phase HLV equilibrium for CO₂-N₂ gas mixture. Fan and Guo [6, 7] have presented hydrate formation data in the presence of water and aqueous sodium chloride solutions (10 wt%) for three CO₂-rich binary gas mixtures (CO₂ + CH₄, CO₂ + C₂H₆, and CO₂ + N₂) and a quaternary gas mixture (CO₂ + CH₄ + C₂H₆ + N₂).

In our laboratory [8], we have studied the CO₂, N₂ and CO₂-N₂ gas mixture by hydrate crystallization and give equilibrium data. For example, the pressure required for CO₂ hydrates formation is about 3.28 MPa at 281.1 K and 35.16 MPa for N₂ hydrates at the same temperature [3]. The equilibrium hydrate formation pressure of CO₂-N₂ mixture is between those of pure CO₂ and pure N₂. Other authors have studied other different gas hydrates mixtures. In 1949, Unruh and Katz [9] studied CO₂-CH₄ gas mixture and obtained some equilibrium data. Adisasmito *et al* [10] have investigated three phase equilibria conditions of CO₂-CH₄ mixtures in the temperature range of 273-288 K and the pressure range of 1.2-11.0MPa. In 2002, Hachikubo *et al* [11], obtained hydrate equilibrium lines of pure carbon dioxide, methane and their mixtures. Most recently, Servio *et al* [12] developed a new experimental technique to measure the mole fraction of gases in the hydrate phase and presented some equilibrium data for CO₂-CH₄ gas mixture. Nevertheless, very few data have been presented to report the equilibrium that means a measurement of both the gas and the hydrate composition.

From the results of these different studies, it is evident that the principal difficulty to envisage a

separation based on hydrate crystallization is the required high formation pressure. To reduce this pressure, it is necessary to use thermodynamic additives such as quaternary ammonium salts [8].

Quaternary ammonium semi-clathrates

Quaternary ammonium salts form, in presence of water, and without any gas, a semi-clathrates hydrate crystal, even at atmospheric pressure [13]. They have been extensively studied in reason of a direct application for air conditioning as a phase change material [2, 14, 15, 16, 17, 18 and 19]. Tetra butyl ammonium bromide salt forms at least four different structures (figure 1) with hydration number of 24, 26, 32 and 36 [13].

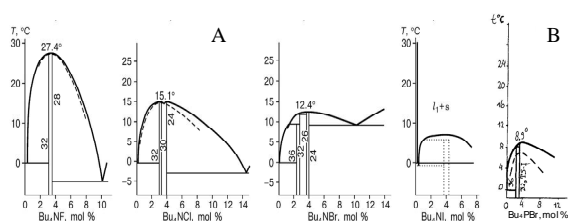


Figure 1: A) T, X – Phase diagram of tetra-n-butyl ammonium salts (respectively fluoride, chloride, bromide and iodide) hydrates [20].

B) T, X – Phase diagram of tetra-n-butyl phosphonium bromide. [21] The values along the lines of composition are the hydration numbers

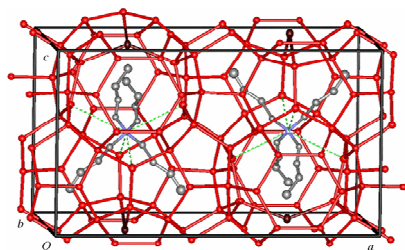


Figure 2: Structure of type B of TBAB hydrates [22].

The crystallographic structure of semi-clathrates hydrates has been determined by McMullan and Jeffrey [12] and completed by Shimada [22]. The TBAB semi-clathrates are different from pure water gas hydrate because bromides participate in the water network and also N^+ cations which are located at the intersection of four cavities [22].

Figure 2 describes the unit cell indicated by solid lines. Bromide atoms and water molecules form

the cage structure. Tetra-n-butyl ammonium is located at the centre of four cages, where the dashed lines represent the broken edges of former gas hydrates cavities.

Oyama *et al* [15] reported some thermal properties of TBAB semi-clathrates. They determined the phase diagram of semi-clathrates hydrates under the conditions of atmospheric pressure, and also measured latent and specific heats capacity. From the phase diagram, the congruent melting points of two different TBAB semi-clathrates structures were determined (12°C and 9.39°C for semi-clathrates with respectively a hydration numbers of 26 and 38).

Pure Gas TBAB semi-clathrates

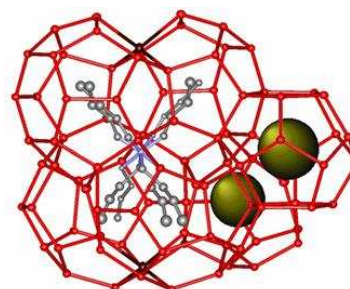


Figure 3: Structure of gas TBAB semi-clathrates [22].

Davidson [23] suggested that these semi-clathrates crystals do not encage gas molecules, but Shimada *et al* [22] and Duc *et al* [8] have given opposite results or opinions.

Shimada *et al* [22, 24] has supposed that TBAB semi-clathrates can encage small gas molecules. In fact, based on the structure analyze of pure TBAB semi-clathrates (formula $(n\text{-C}_4\text{H}_9)_4\text{N}^+\text{Br} 38\text{H}_2\text{O}$), they supposed that the structure can encapsulate the gas in the free cavities (Figure 3, [22]). Duc *et al* [8] have experimentally confirmed that semi-clathrates can encapsulate around 40 m^3 STP of gas per cubic meter of solid. In 2008, Lin *et al* [17] investigated equilibrium conditions and dissociation enthalpy of hydrates formed from CO_2 -TBAB (tetra-n-butyl-ammonium-bromide) water mixtures. Differential Thermal Analysis (DTA) was used for hydrate-liquid-vapor (H-L-V) with a TBAB concentration range from 4.43 to 9.01 wt% and a CO_2 pressure range from 0.3 to 2.5 MPa. The results showed that the presence of TBAB allowed decreasing the formation pressure of CO_2

hydrates by approximately 74% and 87% at 283K and 279 K, respectively. Moreover, the reduction of pressure depends on the TBAB concentration. The dissociation enthalpy and the composition of hydrate formed from 9.01 wt% TBAB solution were determined from both the DTA and the Clapeyron equation.

Deschamps and Dalmazzone [25] studied the dissociation enthalpies and the phase equilibrium of TBAB-gas semi-clathrates hydrates by differential scanning calorimetry (DSC) under pressure. Pure gases such as N_2 and CO_2 and gas mixtures such as N_2 - CO_2 and CH_4 - CO_2 were studied. They presented the phase diagram of N_2 -TBAB semi-clathrates hydrates for different gas pressures, in the TBAB concentration range from 17.0 to 40.0 wt%. Enthalpies of dissociation of TBAB semi-clathrates hydrates of pure gas and gas mixtures were determined as a function of the pressure.

Arjmandi *et al* [18] have proposed equilibrium data for pure gas semi-clathrates of TBAB by using visual observation of the dissociation. They present phase boundaries data on high pressure TBAB (10% wt), TBAB (10% wt)-Nitrogen, TBAB (42.7% wt)-Carbon dioxide, TBAB (5, 10, 20, 30% wt)-Methane, and TBAB (5, 10, 43% wt)-natural gas semi-clathrates.

Tetra-n-butyl ammonium chloride (TBACl) hydrate also has empty cages that can be used for gas capture like TBAB. Makino *et al* [26] have shown that TBACl can be used with H_2 , N_2 , CH_4 , CO_2 and C_2H_6 . The TBACl + CO_2 hydrate is more stable than the corresponding hydrate with TBAB with the hydrate being stable between 16 and 20°C in the same pressure range of TBAB.

EXPERIMENTAL PROCEDURE AND SET-UP

Experimental set-up

An experimental apparatus (figure 4) has been built to investigate the gas hydrates formation and dissociation with and without TBAB. The thermodynamic equilibrium conditions have been obtained by determining pressure and temperature, but also the composition of all liquid and hydrate phases. The experimental set-up is a stainless steel high pressure batch reactor (Autoclave) with a measured volume of $2.51L \pm 0.03$. It is surrounded with a double jacket connected to an externally cooler (HUBERT CC-

505) with a controller CC3 of 0.02 K precision. Two sapphire windows of (12 x 2 cm) mounted on both sides of the reactor allow the visual observation of the hydrates. A Pyrex cell is located in the stainless steel autoclave in which the pressure can be raised up to 10 MPa. The Pyrex cylinder is filled with a volume of 1 L of water containing TBAB at concentration between 5 wt% and 40 wt%. The liquid is injected in the pressurized reactor by using a HPLC pump (JASCO-PU-1587). A four vertical-blade turbine impeller ensures stirring of the suspension during crystallization. Temperature is monitored by two Pt100 probes in the bulk and the gas phases. Pressure is measured by mean of a pressure transducer (range: 0–10 MPa) with a precision of ± 0.05 MPa. The data acquisition unit (P, T) is connected to a personal computer.

A classical valve is used to take a sample of 1ml of liquid. It is analyzed by refractometry to determine either the TBAB or the TBACL concentration.

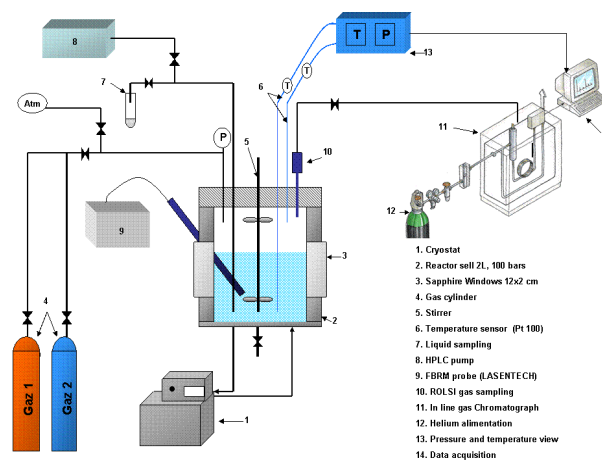


Figure 4: Experimental set-up

Experimental procedure

The hydrate is obtained by crystallization of pure gases (N_2 , CO_2 , and CH_4) with a liquid phase containing water and the salt.

At the beginning, the reactor is closed and vacuumed with a vacuum pump then the cell is flushed three times with N_2 , CO_2 or CH_4 depending on the gas studied. It erases any trace of other gases used in a previous experiment. Then, the reactor is vacuumed again.

After, the reactor is pressurized with the gas. The gas phase is stirred and cooled down and then

maintained at the operative temperature (typically in the range of 278 to 286 K). The temperature need to be higher than the pure TBAB semi-clathrates equilibrium temperature, and lower than pure water gas hydrate equilibrium temperature to be sure that we form gas-TBAB semi-clathrates and not pure water gas hydrates or pure TBAB semi-clathrates.

The stirrer is stopped and the liquid solution (1L) is injected in the reactor by using the HPLC pump. An increase of temperature and pressure is simultaneously observed, firstly because the liquid is at ambient temperature, and also due to the gas compression resulting from the reduction of the gas volume by liquid. The stirrer is started the pressure decreases due to gas dissolution in the liquid.

After a while (from some minutes to several hours, nucleation being a stochastic phenomena), crystallization begins. This is accompanied by a sudden increase of temperature (figure 5). During crystallization (exothermic process), the pressure decreases due to gas consumption by hydrates and the temperature returns to the operative temperature. After a while, the system reaches the equilibrium (end of crystallization), the pressure and the temperature reach constant values.

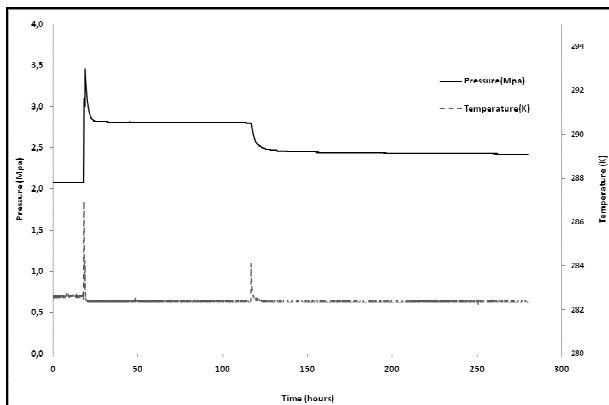


Figure 5: typical example of the evolution of pressure and temperature during crystallization of pure gas -TBAB semi-clathrates

We can proceed to gas hydrate dissociation by two different ways. First way is called isochoric heating. The temperature of the reactor is heated by steps of 1K (figure 6). During each step, the pressure increases due to gas hydrate dissociation and reaches a

constant value which represents the thermodynamic equilibrium.

The second method, called isothermal depressurization consists in depleting the pressure by opening the reactor and waiting for a new equilibrium point. Each step of depressurization is approximatively 0.2MPa. The temperature is controlled and maintained at constant value.

During the dissociation, the liquid is analyzed by refractometry to evaluate the quaternary ammonium concentration.

This procedure is the same in the case of TBACl.

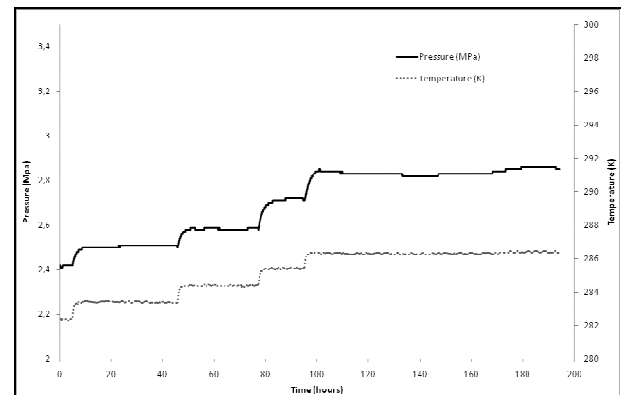


Figure 6: typical example of the evolution of pressure and temperature during dissociation of pure gas -TBAB semi-clathrates

RESULTS AND DISCUSSIONS

N_2 -TBAB semi-clathrates

In this section we present a comparison between the equilibrium data from literature and two experimental points from our work: by using Differential Scanning Calorimetry, Deschamps and Dalmazzone [24] have reported 5 equilibrium points with TBAB concentration of 40% Mass. Two additional points at a same TBAB concentration (40 % Mass TBAB) have been reported by Duc *et al* [8] by using the same experimental procedure of this publication. Lin *et al* [17] reported 7 experimental points at TBAB concentration of 10% Mass. Duc *et al* [8] reposted two other points at 5% Mass TBAB. In this work, we add two new points with TBAB concentration of 20.2% and 24.5%. The data are reported in the following table 2 and plotted in figure 7.

Figure 7 plots the logarithm of pressure versus inverse of the temperature. All the points are reasonably aligned. It reveals that the hydrate structure behaves the Clausius-Clapeyron equation which is normally dedicated to pure components. In fact, if the volume of semi-clathrates approximates that of the liquid solution, then in a good approximation the variation of volume accompanying the crystallization is $\Delta V = V_g = zRT/P$ (z is the compressibility) and we get the famous Clausius Clapeyron relation:

$$\frac{d \ln P}{d(1/T)} = \frac{\Delta H}{zR} \quad (1)$$

TBAB Molar Mass fraction	Equilibrium Temperature [K]	Equilibrium Pressure [MPa]	reference
0.05	279.3	0.67	[8]
0.05	279.8	1.09	
0.40	285.15	4.44	
0.40	286.15	4.68	
0.65	284.0	2.90	
0.40	285.99	6.27	[23]
0.40	286.75	7.16	
0.40	287.75	8.31	
0.40	288.08	9.84	
0.40	291.6	20.49	
0.10	285.99	6.27	[18]
0.10	286.75	7.16	
0.10	287.75	8.31	
0.10	288.08	9.84	
0.10	291.6	20.49	
0.10	285.99	6.27	
0.10	286.75	7.16	
0.10	287.75	8.31	
0.20	287.95	7.61	This work
0.24	288.85	8.36	

Table 2 N₂-TBAB semi-clathrates. Experimental equilibrium data from literature and additional point from this work

By plotting $\ln P$ versus $1/T$ (figure 7), we observe a linear behavior which allows to suppose that a common structure is crystallized whatever the temperature. But, more surprising, it reveals also that the pressure is first order dependent on the temperature only, and not on the TBAB concentration. Normally, the equilibrium pressure is dependent also on the salt concentration

because the chemical potential of water varies in proportion of the salt concentration. Here, it seems to not be the case, or at least, it seems that the equilibrium pressure is dependent on the salt concentration at an order that cannot be evaluated in respect to the precision of the data. This observation is different from the ones we will show in the next part of the work about CO₂ and CH₄ pure gas semi-clathrates. We will see later that, for CH₄ and CO₂ pure gas semi-clathrates, the equilibrium pressure is clearly dependent on both the temperature and TBAB concentration. But, for N₂ pure gas semi-clathrates, the equilibrium pressure is first order on the temperature only.

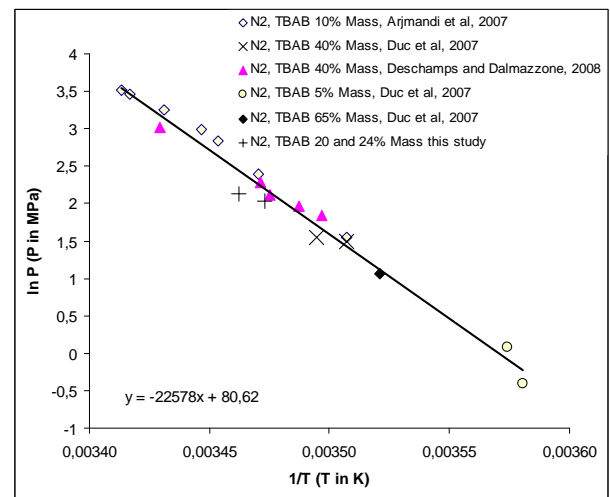


Figure 7 N₂-TBAB semi-clathrates. Experimental equilibrium data from literature and additional point from this work

CH₄-TBAB semi-clathrates

The literature survey allows completing our experimental results (Table 3) with the data of Arjmandi *et al* [18]. They give a complete work of the influence of the pressure-temperature dependency over TBAB concentration of 5%, 10%, 20% and 30% wt. By plotting their results in a $(\ln P, 1/T)$ diagram, we get a classical Clausius-Clapeyron behavior. Assuming a common semi-clathrates structure, independently of the TBAB concentration, the equilibrium data can be fitted by a linear shape ($y=A \cdot x+B$) and constant slope of $A=-26999$ (figure 8). It confirms that the semi-clathrates structure remains constant over temperature and TBAB concentration. But, at the difference of the

previous N₂-TBAB semi-clathrates equilibrium data, we can observe the TBAB concentration affects the equilibrium.

The B value can be interpolated under the following form:

$$B = -0.0028 / x_{TBAB}^2 + 0.1492 / x_{TBAB} + 93.429 \quad (2)$$

where x_{TBAB} is the TBAB mass fraction.

%mass TBAB	Equilibrium Temperature [K]	Equilibrium Pressure [MPa]	This work
0.020	280.0	3.17	
0.024	280.0	2.66	
0.027	280.0	2.15	
0.028	280.0	1.77	
0.029	280.0	1.42	
0.033	280.0	1.09	
0.045	280.0	0.82	
0.049	280.0	0.63	
0.055	280.0	0.54	
0.060	282.0	1.00	
0.066	282.0	0.82	[27]
0.074	282.0	0.68	
0.083	282.0	0.54	
0.093	282.0	0.39	
0.027	280.8	3.60	
0.033	283.4	3.70	
0.039	284.8	3.77	
0.056	285.4	4.69	
0.060	287.6	4.83	
0.077	288.7	4.95	
0.092	289.6	5.10	
0.156	289.2	3.40	[28]

Table 3 CH₄-TBAB semi-clathrates.

Experimental equilibrium data from literature and additional point from this work

From our experimental results (Table 3), we also evaluated the B value for each x_{TBAB} , and we report on figure 9 B versus x_{TBAB} (A value is assumed to be $A=-26999$). We can see that, up to $1/x_{TBAB}$ value of 15, experimental results from Arjmandi *et al* [18] and our data fit well. It signifies we get the same equilibrium data. But, for higher values, which correspond to $x_{TBAB}<0.05$, we can see a difference between the B values, and so a difference between our equilibrium points and data reported by Arjmandi *et al* [18]. This difference can be due to a mistake in the measurements. But, we will see in the next part about the CO₂-TBAB that semi-clathrates

can present different polymorphs at a same TBAB concentration. So, the difference between the equilibrium points from our work and from literature could also be explained by a difference between the polymorphs that have been crystallized in both the laboratories.

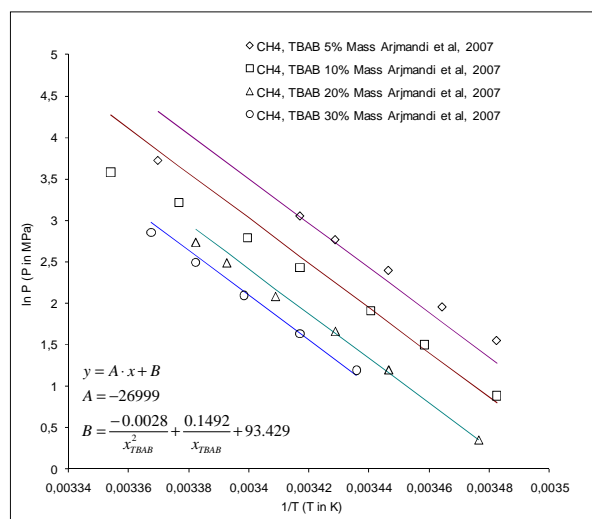


Figure 8 CH₄-TBAB semi-clathrates. Equilibrium data from Arjmandi *et al* [18].

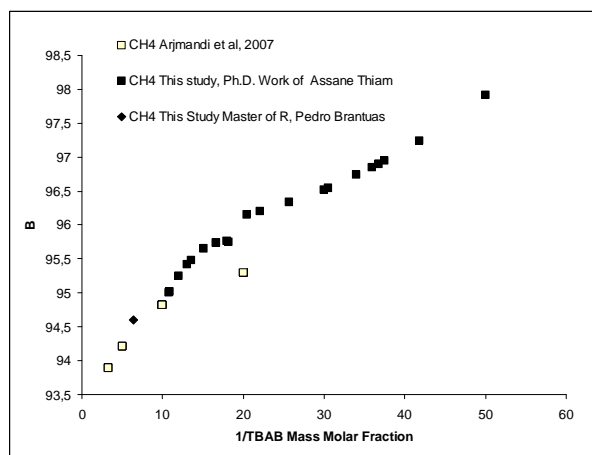


Figure 9 CH₄-TBAB semi-clathrates. Value of the B constant in the equation $\ln P = -26999/T + B$.

CO₂-TBAB semi-clathrates

We present our experimental data on Table 4. The literature survey allows completing with experimental points from Lin *et al* [17]. They give a complete work of the influence of the pressure-temperature dependency over TBAB

concentration of 4%, 7% wt and 9% wt. It can be completed with data from Deschamps and Dalmazzone [25], Arjmandi *et al* [18] and Duc *et al* [8]. Each of these authors has given data for a TBAB concentration of 40% wt. The figure 10 assumes a common structure and plot $\ln P$ versus $1/T$. We can conclude that data can be fitted assuming a linear shape ($y=A \cdot x+B$) and constant slope $A=-27337$. It confirms that the semi-clathrates structure remains constant over temperature. The A value is much closer to the value obtained for CH_4 hydrate ($A=-26999$), and we can suspect the structures to be the same. The B value can be interpolated under the following form

$$B = 0.002936/x_{\text{TBAB}}^2 - 0.003785/x_{\text{TBAB}} + 9536 \quad (3)$$

where x_{TBAB} is the TBAB mass fraction.

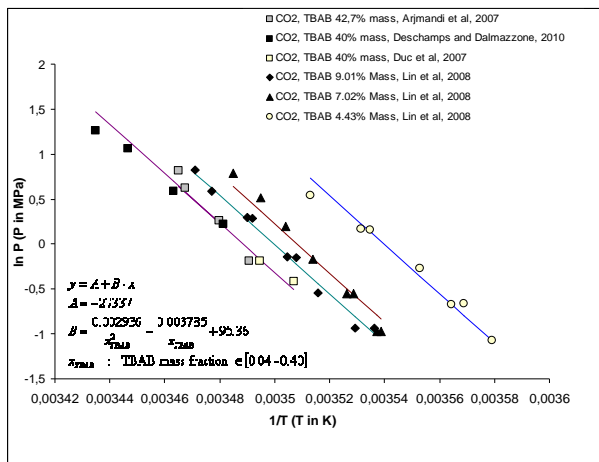


Figure 10 CO_2 -TBAB semi-clathrates. Equilibrium data from literature.

This B value calculated from equilibrium (P, T) data from literature have been compared to the ones calculated from our experimental results. We assume $A=-27337$. The B value for each x_{TBAB} value is reported on figure 11. It appears two curves which physical signification is the co-existence of two different structure (or polymorphs). The upper curve corresponds mainly to the data we obtained in this work by using the dissociation method called isothermal depressurization, plus two points obtained from the other method called isochoric heating. By using the second method, practically all the points, except two, are aligned on the downer curve. The downer curve corresponds also to the

curve on which are aligned the data from the literature. A very interesting observation concerns one of the isochoric depressurization which shifts from the downer curve to the upper one. It is characteristic to a transition from a polymorphic structure to another one. So the figure 11 puts into evidence the existence of two polymorphic structures with different equilibrium curves.

%mass TBAB	Equilibrium Temperature [K]	Equilibrium Pressure [MPa]	This work	
Dissociation Data from Isothermal depressurization				
0,027	280,0	1,43	[27]	
0,032	280,0	1,13		
0,038	280,0	1,00		
0,041	280,0	0,83		
0,043	280,0	0,71		
0,044	280,0	0,60		
0,050	280,0	0,49		
0,056	280,0	0,38		
0,000	282,0	1,07		[27]
0,059	282,0	0,87		
0,061	282,0	0,68		
0,067	282,0	0,54		
0,077	282,0	0,41		
0,088	282,0	0,33		
0,093	282,0	1,07		
Dissociation Data from isochoric heating				
0,032	280,5	1,47	[27]	
0,037	282,6	1,57		
0,040	283,7	1,63		
0,043	284,9	1,70		
0,054	282,8	1,28	[27]	
0,058	283,7	1,34		
0,072	285,1	1,47		
0,093	286,8	1,54		
0,173	285,3	0,85		[28]
0,197	285,9	0,91		
0,226	286,7	1,04		
0,237	287,5	1,26		

Table 4 CO_2 -TBAB semi-clathrates. Experimental equilibrium data from literature and additional points from this work

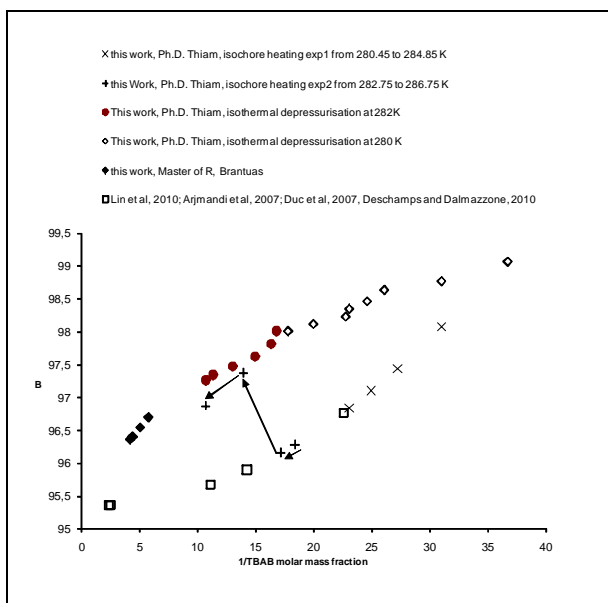


Figure 11 CO₂-TBAB semi-clathrates – Value of the B constant in the equation $\ln P = -27337/T + B$.

CO₂ – Salt semi-clathrates

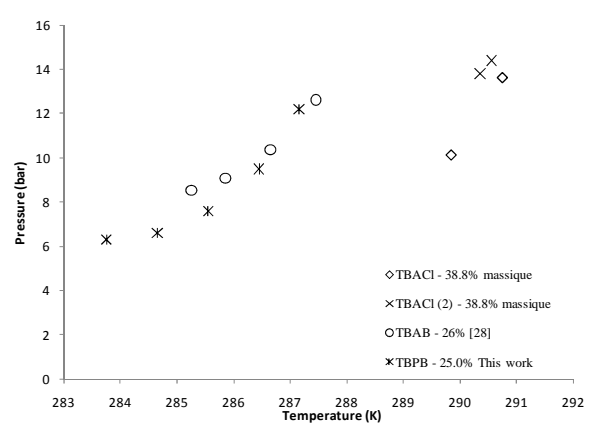


Figure 12 Different salts (TBAB, TBACl and TBPB) – CO₂ hydrates equilibrium conditions in a pressure temperature diagram. The 1 refers to a TBACl experience which started with 15 bar of CO₂ and 2 corresponds to an initial pressure of 20 bar of CO₂.

In figure 12 we can see that TBACl hydrates are more stable than TBAB hydrates at higher pressures and temperatures, while TBPB hydrates are in the same temperature range of TBAB although at a slightly lower pressure. Interesting is the difference between the results for TBACl where the same solution has a different aspect

depending on the initial value of CO₂ in the system.

CONCLUSIONS

In this paper, we presented new experimental data about equilibrium of pure gas hydrates (CO₂, N₂ and CH₄) in presence of the tetra n-butyl ammonium Bromide (TBAB) and we compare our results to literature

Three gas-TBAB semi-clathrates were studied in this work CO₂-TBAB, N₂-TBAB and CH₄-TBAB. In the case of N₂-TBAB semi-clathrates, observations show that the pressure is first order depending on the temperature only and not dependent on the TBAB concentration.

For the CO₂-TBAB and CH₄-TBAB semi-clathrates the results are different. In fact, the equilibrium pressure is clearly dependent on both temperature and TBAB concentration

We compare the experimental results for CH₄ to experimental results of Arjmandi [18] we observe that data fit well for $x_{TBAB} > 0.05$. But for higher values corresponding to $x_{TBAB} < 0.05$, the Arjmandi's data didn't fit our results, this difference can be due to experimental errors or the presence of different polymorphs at same TBAB concentration what we observe in the case of CO₂-TBAB semi-clathrates

Our studies concerning other salts than TBAB are on the beginning phase, therefore we do not have enough data to realize the same study we did in regards of the gas – TBAB semi clathrates. Still this gives us good indications in what to look for in the future and to continue to analyze these types of hydrates.

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