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# CO<sub>2</sub> CAPTURE BY USING HYDRATES:

## 1) THE BENEFICE AND THE COUNTERPART OF THERMODYNAMIC ADDITIVES

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### ABSTRACT

CO<sub>2</sub> capture by using clathrates is a method which benefits from the CO<sub>2</sub> selectivity in gas hydrates to separate it from nitrogen, or other exhaust gases from gas or coal combustion. The bottleneck is the operating pressure which still remains high and needs to drop to 0.5 MPa in order to compete with the reference case using amines. As part of two national projects (SECOHYA, ACACIA) and a European program (iCAP), we tested different classes of thermodynamic additives, organic (water insoluble cyclopentane, water soluble THF) which form classical gas hydrates with structure SII, and ionic (Tetra-N-Butyl Ammonium Bromide, TBAB) which forms new types of structures.

In this presentation, we show experimental results that clearly demonstrate that the operating pressure can be reduced to atmospheric pressure, and we emphasize that the CO<sub>2</sub> selectivity is enhanced, with cyclopentane as an additive, but also especially by using TBAB where the selectivity can be boosted up to 100%.

We also show that the experimental conditions of pressure and temperature need to be selected outside the region of formation of the single additive hydrate. If not, the gas storage capacity drops to a negligible value.

We conclude the presentation by showing the physical impossibility to find a thermodynamic additive to drop the operative pressure without dropping the storage capacity.

*Keywords:* clathrates and semi clathrates hydrates, thermodynamic additives, gas separation

### Introduction

Greenhouse gas emissions have been identified as the major source of global warming. Among the greenhouse gases emitted into the atmosphere due to anthropogenic activities, carbon dioxide (CO<sub>2</sub>) plays a major role. One possible way to reduce the global CO<sub>2</sub> emissions is to establish suitable capture processes that can be integrated in existing plants and equipment and by which carbon dioxide can be removed from the considered flue gas streams. Flue gas mixtures of conventional post-combustion power plants are characterised by low carbon dioxide mole fractions ranging from 0.05 to 0.15. In addition, the respective gas streams are typically emitted at high flow rate. The challenge is to develop CO<sub>2</sub> capture technologies by which

both energetic and capital costs (size of the units) are minimized. An innovative technology for gas separation and capture could be based on a process making use of gas hydrate formation.

For the typical case of a steel making plant, an energetic costing performed by Duc et al (2007) showed that the process making use of the semi-clathrate hydrate approach can be competitive compared to conventional capture technologies. The separation cost is mainly due to the gas compression stages. Hence, the objective is to lower the operational pressure.

We tested different additives as a thermodynamic additive, tetrahydrofuran which is perfectly miscible with water and forms a SII clathrate hydrate (Herslund et al, 2013),

cyclopentane which is not miscible with water and forms also a SII clathrate hydrate (Galfré et al, 2013), and lastly quaternary ammonium salts which form semi-clathrate hydrates (Herri et al, 2014). In each case, we can drop the operating pressure, sometimes we can enhance the selectivity of the CO<sub>2</sub> separation. But also we systematically drop the hydrate storage capacity to a value that is incompatible with an industrial application as explained in the fourth paper of this series of four papers.

### **Tetrahydrofuran: An example of water soluble additive**

Tetrahydrofuran (THF) forms structure II hydrates in which THF occupies the large cavity  $5^{12}6^4$  and gas competes with THF for the occupation of the large cavity and/or occupies the small cavity. THF is a water-soluble additive. With water, they are completely miscible in the liquid state over the whole composition range in the pressure and temperature domain of hydrate formation (Riesco et al., 2005). The equilibrium pressure reduction effect to form hydrates is dependent on the relative concentration of THF. It is important to notice that in presence of pressurized carbon dioxide (temperature above 290 K and a pressure above 2.0 MPa), Sabil et al., 2010 observed that water and THF phase split in two liquid phases (in presence of a solution of 5% mole of THF in water). Over the years, many authors reported hydrate dissociation data of the system {THF + water + gas}. Only works where nitrogen and carbon dioxide were used are presented in the following paragraph.

#### *Benefits of THF on the equilibrium of pure gases:*

Seo et al. (2001, 2008) studied the hydrate dissociation pressure – temperature data {H<sub>2</sub>O + THF + pure gas (CO<sub>2</sub> or N<sub>2</sub>)} for several compositions of THF (1 to 5 %mol of THF in water) and the hydrate dissociation pressure – temperature data {H<sub>2</sub>O + THF + CH<sub>4</sub>} for 3 %mol of THF.

Firstly, their studies focused on showing the stabilization effect of THF on hydrate formation compared to the effect of other water miscible promoters (propylene oxide, 1,4-dioxane, acetone). For a concentration of promoter of 3 %mol, THF was found to be the most interesting for each gas (CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub>).

Secondly, the effect of THF concentration from 1 to 5 %mol on the equilibrium hydrate dissociation pressure-temperature data has been studied. The

pressure decreased rapidly up to 1 %mol of THF, but very slowly above 1 %mol for each case study (CO<sub>2</sub> and N<sub>2</sub>).

Delahaye et al. (2006) also investigated the hydrate dissociation pressure – temperature data {H<sub>2</sub>O + THF + CO<sub>2</sub>} for THF concentration in the range of 1.6 to 3.0 %mol, and the latent heat of dissociation of the mixed hydrates (CO<sub>2</sub>/THF/water). Like Seo et al (2008) the authors observed the drastic reduction of the hydrate pressure formation with a few mole of THF in the system.

Sabil et al. (2010) also examined the complete hydrates dissociation lines for the systems {H<sub>2</sub>O + CO<sub>2</sub>} and {H<sub>2</sub>O + THF + CO<sub>2</sub>} at a THF concentration of 5 %mol for different carbon dioxide concentrations. The authors discovered a four-phase equilibrium region with three fluid phases at temperatures above 290K and pressures above 2.0 MPa : a water-rich with a constant amount of carbon dioxide, a carbon dioxide in an organic-rich, the vapor phase and the hydrate phase.

Finally, Yang et al., 2011 studied the hydrate dissociation pressure – temperature data {H<sub>2</sub>O + THF + pure gas (N<sub>2</sub>)} for THF concentration of 5 %mol. The authors also provided equilibrium phase hydrate data for {O<sub>2</sub> + THF + water}, {air + THF + water}. Their research focused on finding valuable information on the air separation by hydrate crystallization.

#### *Benefits of THF on gas mixtures:*

Recovering CO<sub>2</sub> from a gas mixture of CO<sub>2</sub>/N<sub>2</sub> in presence of THF was the purpose of the works of (Kang and Lee, 2000, 2001 and Linga et al., 2007). The authors measured the hydrate dissociation data for several mixtures of CO<sub>2</sub> and N<sub>2</sub> without any promoter and in presence of THF. As for pure gases, with aqueous solutions containing 1 and 3 %mol of THF, a drastic drop of equilibrium dissociation pressure has been observed from the moment the THF concentration reached 1 mole percent (Kang and Lee, 2000, 2001). Moreover, a benefit of THF is observed on the selectivity of the separation. Pressure-composition diagrams of the {H<sub>2</sub>O + THF + CO<sub>2</sub>/N<sub>2</sub>}. The respective hydrate compositions of the mixed hydrates with and without THF have been added on the diagrams. Kang and Lee (2000) showed that the CO<sub>2</sub> selectivity in the mixed hydrate phase has been lowered in the mixed hydrate when the THF has been used as a hydrate promoter.

Linga *et al.* (2007) tested a THF concentration of 1 %mol and studied the gas uptake and the rate of the crystallization. THF reduced the induction time but also the growth rate of the crystallization.

The authors did not estimate the carbon dioxide selectivity and did not calculate the gas storage capacity.

Finally, Linga *et al.* (2010) investigated the formation of gas hydrate with one composition of gas mixture at THF concentrations of 1 and 1.5 %mol. The authors estimated the gas uptake and the CO<sub>2</sub> recovery and compared them to the results reported in the literature with tetra-n-butyl ammonium bromide and tetra-n-butyl ammonium fluoride (Fan *et al.*, 2009; Li *et al.*, 2009).

### Cyclopentane: an immiscible organic additive

Cyclopentane (CP) is described in the literature as an excellent thermodynamic promoter. It forms structure II hydrate without any gas (Nakajima *et al.*, 2008) but competes with CO<sub>2</sub> to occupy the large cavity 5<sup>12</sup>6<sup>4</sup>. Cyclopentane is a hydrophobic compound and needs to be dispersed in water. So, the main difference with THF is the low solubility of CP in water.

Fan *et al.* (2001) were the first to report the quadruple equilibrium point (CP hydrate-liquid water-organic liquid-vapor) at a temperature of 280.22 K and a pressure of 0.0198 MPa (abs).

As for THF, many authors reported the hydrate dissociation data of the system (THF + water + pure CO<sub>2</sub>, pure N<sub>2</sub>, or CO<sub>2</sub>+N<sub>2</sub>): their works are detailed in the following paragraph.

Zhang *et al.* (2009a, b) determined hydrate dissociation data for {H<sub>2</sub>O + CO<sub>2</sub>+CP} system. Dissociation conditions for {H<sub>2</sub>O + CO<sub>2</sub>+CP} hydrate have been compared with the dissociation data for {H<sub>2</sub>O + CO<sub>2</sub>+TBAB} with a TBAB weight fraction of 0.427 (Arjmandi *et al.*, 2007) and for {H<sub>2</sub>O + CO<sub>2</sub>+THF} with a THF molar fraction of 3 percent (Delahaye *et al.*, 2006). CP appears to be a better additive than TBAB to decrease the equilibrium pressure.

Zhang & Lee (2009c) also studied the potential of using CP as a kinetic promoter in a static autoclave at a low temperature.

Mohammadi *et al.* (2010) compared the stabilization effect of CP on hydrate formation of {H<sub>2</sub>O + CO<sub>2</sub>+CP} gas hydrate to the effect of several organic promoters (example: methyl-cyclopentane, methyl-cyclohexane, and cyclohexane). For volume fraction of promoter of 10% in water, among the promoters, CP promotion

effect was the highest. Experimental dissociation data for clathrate hydrates of cyclopentane and carbon dioxide have been also reported. Data were in good agreement with the study of Zhang *et al.* (2009a, b).

Experimental hydrate dissociation data for {H<sub>2</sub>O + N<sub>2</sub>+CP} system were first published by Tohidi *et al.* (1997). They tested the potential of using cyclopentane to decrease the equilibrium pressure when gas hydrates of nitrogen and promoter (cyclopentane or neopentane) are formed. CP promotion effect has also been compared in that case to several organic promoters of the literature (cyclohexane and benzene). It was found to be the strongest promoter, just above neopentane.

Mohammandi *et al.* (2011) and Du *et al.* (2010) completed the experimental hydrate dissociation data for {H<sub>2</sub>O + N<sub>2</sub>+CP} system and there results were in good agreement.

For CO<sub>2</sub>/N<sub>2</sub> gas mixture, Li *et al.* (2010) preliminary showed that gas hydrates could be enriched in CO<sub>2</sub> in presence of cyclopentane. The authors studied two different situations: CP dispersed in an emulsion or a buoyant CP phase on the top of the liquid water phase. Differences in the separation efficiency have been reported. This difference implies that the authors have not reached the thermodynamic equilibrium in their work. In fact, we will comment this point in our discussion, but it appears that the formed hydrate from a gas mixture are not at equilibrium, and that its composition is directly dependent on kinetic considerations, and so is indirectly dependent on the geometry of the system.

Galfré *et al.* (2014) shows the “selectivity curve” (Figure 1) in which for the system {H<sub>2</sub>O + CP + CO<sub>2</sub> + N<sub>2</sub>} under the condition of H-L<sub>w</sub>-L<sub>hc</sub>-G four phase equilibrium, the binary mole fraction of CO<sub>2</sub> in the mixed CO<sub>2</sub> + N<sub>2</sub> + CP hydrate phase,  $z'_{CO_2} = n_{CO_2}^H / (n_{CO_2}^H + n_{N_2}^H)$ , is plotted against the binary mole fraction of CO<sub>2</sub> in the gas phase  $y'_{CO_2} = n_{CO_2}^G / (n_{CO_2}^G + n_{N_2}^G)$ . This curve covers the temperature range from 283.5 K to 287.5 K and the pressure range from 0.76 MPa to 2.23 MPa. In addition to the experimental data, Figure 1 shows corresponding curves calculated via a simulation for the system without cyclopentane, i.e. for the system {H<sub>2</sub>O + CO<sub>2</sub> + N<sub>2</sub>}, by means of the in-house

programme “GasHyDyn” (Herri et al, 2011) at four different temperatures  $T$ .

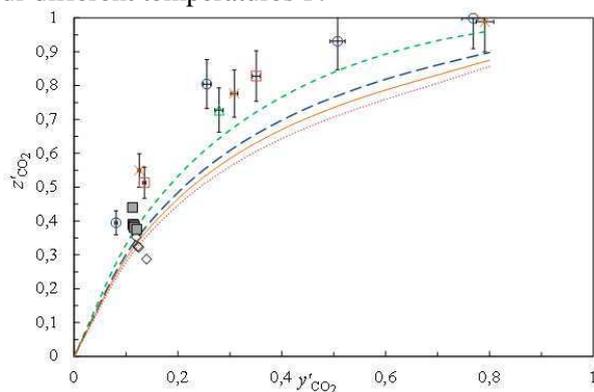


Figure 1. Mole fraction of  $\text{CO}_2$  in the hydrate phase  $z'_{\text{CO}_2}$  as function of the corresponding mole fraction of  $\text{CO}_2$  in the gas phase  $y'_{\text{CO}_2}$ , both at equilibrium, for different temperatures  $T$  between 282.5 K to 287.5 K. Symbols correspond to experimental data at ( $\Delta$ ) 282.5 K, ( $\circ$ ) 285.3 K, ( $\times$ ) 286.2 K and ( $\square$ ) 287.3 K. Literature data of Li et al. (2010) for ( $\diamond$ ) emulsion system, and ( $\blacksquare$ ) system containing two “macroscopic” liquid phases. Simulations obtained by means of the in-house software “GasHyDyn” (Herri et al, 2011) for the corresponding system without cyclopentane at (----) 282.5 K, (- - -) 285.3 K, (—) 286.2 K and (.....) 287.3 K.

It can be seen in Figure 1 that the carbon dioxide selectivity in the mixed  $\text{CO}_2 + \text{N}_2 + \text{CP}$  hydrates is significantly increased compared to the theoretical selectivity of the gas hydrates without any promoter. For example, the mole fraction of  $\text{CO}_2$  relative to the system  $\{\text{CO}_2 + \text{N}_2\}$  present in the hydrate phase  $z'_{\text{CO}_2}$  approaches 0.931 for a corresponding mole fraction of  $\text{CO}_2$  in the gas phase  $y'_{\text{CO}_2}$  of 0.507.

Experimental data presented by Li et al. (2010) for mixed  $\text{CO}_2 + \text{N}_2 + \text{CP}$  hydrates are also reported in Figure 1. and appear to give a lower selectivity. In their article, Galfré et al (2013) argued that the data of Li et al. (2010) are not at equilibrium and cannot directly be compared to the data presented in their work.

In Figure 2, the gas storage has been reported by Galfré et al (2014) against the composition of the  $\text{CO}_2 + \text{N}_2$  gas phase in terms of  $y'_{\text{CO}_2}$ . In this diagram, it can be seen that the Gas Storage

Capacity is in the range of  $(20\text{--}60) \text{ m}^3 \text{ gas.m}^{-3} \text{ hydrate}$ , scattered around a mean value of  $40 \text{ m}^3 \text{ gas.m}^{-3} \text{ hydrate}$ .

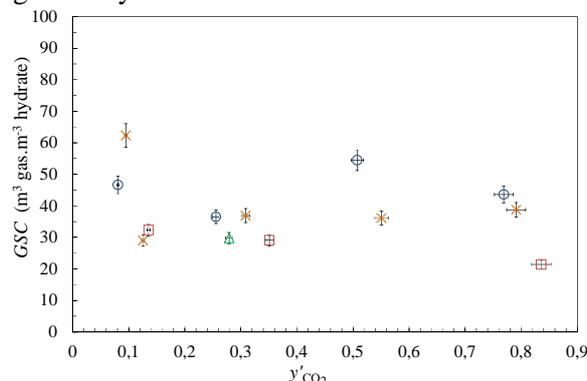


Figure 2. Gas storage capacity for  $\text{CO}_2 + \text{N}_2$  gas mixtures from 282.5 K to 287.5 K as function of the mole fraction of  $\text{CO}_2$  in the gas phase  $y'_{\text{CO}_2}$  (with respect to the total amount of  $\text{CO}_2 + \text{N}_2$ , i.e.,  $y'_{\text{CO}_2} + y'_{\text{N}_2} = 1$ ). Symbols correspond to experimental data at ( $\Delta$ ) 282.5 K, ( $\circ$ ) 285.3 K, ( $\times$ ) 286.2 K, ( $\square$ ) 287.3 K.

Lastly, Herslund et al (2013) have reported that below 281 K, we can observe a competition in between the crystallization of pure cyclopentane sII hydrates and mixed carbon dioxide–cyclopentane hydrates. It is due to the stability of pure CP clathrate hydrate, and contributes significantly to decrease again the storage capacity if the temperature is decreased too much.

### Semi clathrate hydrates

Another class of clathrates, called semi-clathrates, can be formed in presence of electrolytes, such as alkyls Ammonium salts or alkyls Phosphonium salts (Sato et al, 2013). It forms, in presence of water, and without any gas, a semi-clathrates hydrate crystal, even at atmospheric pressure (McMullan and Jeffrey, 1959). They are qualified as peralkylonium polyhydrates and have been the research project of the Russian team of Dyadin and co-workers over decades and were only published in English in 1984, 1985 and 1995. In contrast to gas hydrates, the cation is the guest situated in the framework cavities and separated from the host- molecules by the distance not less than the sum of the Van der Waals radii (Dyadin and Udachin, 1984).

So, they are called semi-clathrates due to the fact that the crystalline water network is broken in order to incorporate the cation of the compound. For instance, in the case of TBAB hydrate, the

nitrogen atom at the center of the four butyl radicals takes the place of a water molecule effectively, “breaking” the four surrounding cages and creating a larger cavity made from smaller ones. Therefore the hydration number will change regarding gas hydrates because less water molecules in a similar structure, due to their replacement by the cation of the semi-clathrate, will be present. Bromide atoms and water molecules form the cage structure. Tetra-*n*-butyl ammonium is located at the centre of four cages (Shimada *et al.*, 2005b) and the butyl groups occupy the cavities. There is a large number of semi-clathrate compounds due to the different cation and anion they possess (Herri *et al.*, 2014)

With a wide range of anions and cations that can compose a semi-clathrate, it is not a surprise that many different crystalline structures can be formed. A detailed review has been made by Dyadin and Udachin in 1987 which continues to be the reference on the subject.

Tetra-*N*-Butyl ammonium Bromure has been extensively studied in reason of a direct application for air conditioning as a phase change material (Lipkowski *et al.*, 2002, Oyama *et al.*, 2005, Kamata *et al.*, 2004, Darbouret *et al.* 2005, Lin *et al.*, 2008, Arjmandi *et al.*, 2007 and Li *et al.*, 2009). Tetra butyl ammonium bromide salt forms at least four different structures with hydration number of 24, 26, 32 and 36 (Lipkowski *et al.*, 2002). Only one of the crystallographic structures of semi-clathrate hydrates has been determined precisely by McMullan and Jeffrey (1959) and completed by Shimada (2005b). A complete reviewing off all the equilibrium data can be in Sato *et al.* (2013)

Davidson (1973) suggested that these semi-clathrates crystals do not encage gas molecules, but Shimada *et al.*, (2005a) and Duc *et al.*, (2007) have given opposite results or opinions. Shimada *et al.*, (2003, 2005a) has supposed that TBAB semi-clathrates could encage small gas molecules. In fact, based on the structure analyze of pure TBAB semi-clathrates (formula  $(n-C_4H_9)_4N^+Br^- \cdot 38H_2O$ ), they supposed that the structure could encapsulate the gas in the free cavities (Figure 3). Duc *et al.*, (2007) have experimentally confirmed that semi clathrates can encapsulate up to 40 M<sup>3</sup> STP of gas per cubic meter of solid.

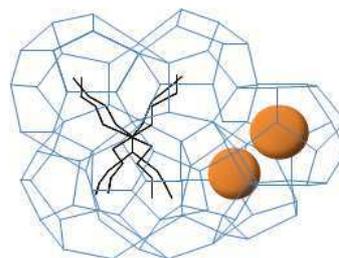


Figure 3 : Structure of gas TBAB semi-clathrates (Shimada *et al.*, 2005b).

Since this period, a huge quantity of experimental results have been produced which gives evidence of the enclathration of gases in the TBAB structure. The question that remains is which structure is formed. In fact, facing the variety of possibilities, and except the work of Shimada *et al.*, (2005b) who clearly identified one structure in presence of gas, we do not have evidence of the crystallographic structure formed.

#### **(Pressure-Temperature) equilibrium with TBAB, CO<sub>2</sub> and N<sub>2</sub>**

In recent years, many experimental data have been produced about the equilibrium of TBAB semi-clathrate in presence of pure CO<sub>2</sub> and pure N<sub>2</sub> gas. Also, a model has been produced by Paricaud (2011) to predict the pressure and temperature of equilibrium as a function of the TBAB mass fraction for only one type of hydrate structure. Arjmandi *et al.*, (2007) have given CO<sub>2</sub>-TBAB semi clathrate equilibrium data at TBAB mass fraction of 0.1 and 0.4. Duc *et al.*, (2007) have determined few points at TBAB mass fraction of 0.05, 0.09, 0.5 and 0.65. Lin *et al.*, (2008) did a complete study for TBAB mass fraction of 0.044, 0.07 and 0.05. Oyama *et al.*, (2008) gave equilibrium data of CO<sub>2</sub> semi clathrate at TBAB mass fraction of 0.1. But also, they produced data at very low mass fraction of 0.01, 0.02, 0.03 and 0.045 without formation of the semi clathrate hydrate but only formation of the clathrate hydrate. Lastly, Deschamps and Dalmazzone (2009) have given few points at TBAB mass fraction of 0.4.

Experiments about N<sub>2</sub>-TBAB semi clathrate equilibrium are less numerous. Arjmandi *et al.*, (2007) have given N<sub>2</sub>-TBAB semi clathrate equilibrium data at TBAB mass fraction of 0.1. Duc *et al.*, (2007) have determined few points at TBAB mass fraction of 0.05, 0.09, 0.5 and 0.65. Deschamps and Dalmazzone (2009) have given few points at TBAB mass fraction of 0.4.

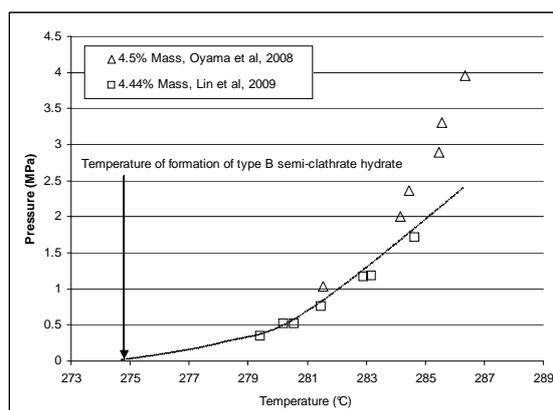


Figure 4: CO<sub>2</sub>-TBAB semi clathrate equilibrium curve at TBAB mass fraction of 4.44-4.5%, from Oyama *et al.* (2008) and Lin *et al.* (2009)

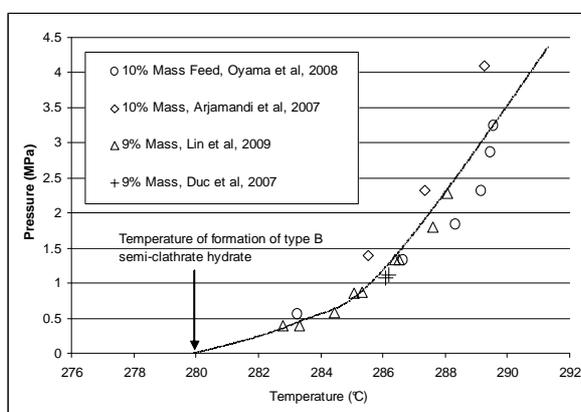


Figure 5: CO<sub>2</sub>-TBAB semi clathrate equilibrium curve at TBAB mass fraction of 9-10 percent, from Arjmandi *et al.* (2007), Duc *et al.* (2007), Oyama *et al.*, 2008 and Lin *et al.* (2009)

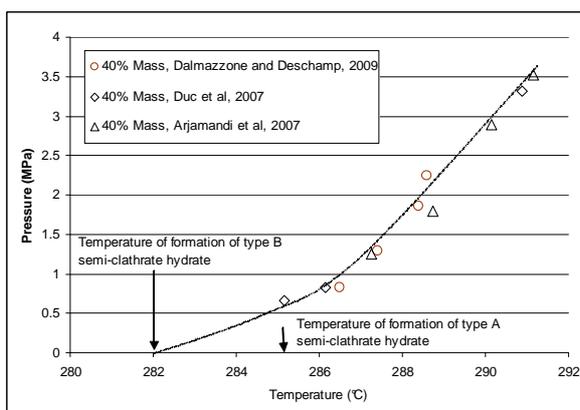


Figure 6: CO<sub>2</sub>-TBAB semi clathrate equilibrium curve at TBAB mass fraction of 40 percent, from Arjmandi *et al.*, 2007, Duc *et al.*, 2007, Dalmazzone and Deschamps, 2009

Figure 4, Figure 5 and Figure 6 show some of the experimental data for CO<sub>2</sub>-TBAB semi clathrate. All the data are not coherent. On Figure 4, for two similar TBAB mass fractions, we can distinguish two different equilibrium curves (Oyama *et al.* in 2008, and Lin *et al.* in 2009). At TBAB mass fraction of 9-10 percent (Figure 5), the equilibrium data of Arjmandi *et al.*, (2007), Duc *et al.*, (2007), Oyama *et al.*, (2008) and Lin *et al.*, (2009) do not seem in coherence together. But, at TBAB mass fraction of 0.4 (Figure 6), the data from Arjmandi *et al.*, (2007), Duc *et al.* (2007) and Dalmazzone and Deschamps (2009) appear to be coherent together. The difference between the authors can be explained by the difficulty to crystallize the same structure. In fact, as we underlined before, the TBAB semi-clathrate can crystallize under 4 structures, and at least two of them can capture gas (Paricaud, 2009).

Independently of the difference between the experiments, it can be stated that the equilibrium pressure decreases as the temperature decreases. The different authors reported equilibrium pressure down to 0.5 MPa, but never close to the atmospheric pressure. In fact, at low pressure, the kinetics slow down and the crystallization time becomes too much long to be observed. But, from a theoretical point of view (Herri *et al.*, 2014), the equilibrium pressure tends to 0 as the temperature tends to the temperature of equilibrium of the pure TBAB clathrate hydrate.

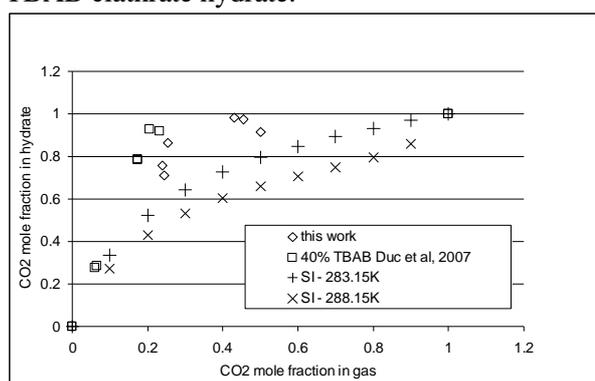


Figure 7: Selectivity of the separation of CO<sub>2</sub> from N<sub>2</sub> during crystallization of semi-clathrate hydrates from TBAB solution, and comparison to the selectivity of clathrate hydrate of structure SI.

Figure 7 presents the selectivity of the separation of CO<sub>2</sub> from N<sub>2</sub> during crystallization of semi-clathrate hydrates from TBAB solution, from Herri

et al (2014). The data from this work are compared to the results from Duc *et al.*, (2007). All the experimental points of this study and from Duc *et al.*, (2007) are in the range of temperature [283.4-288.6K]. Herri et al (2014) plotted a reference case consisting in the molar fraction of CO<sub>2</sub> in the SI structure (pure water clathrate hydrate), at two temperatures of 283.15K and 288.15 K. We can observe an enhancement of the content in CO<sub>2</sub> in the case of the semi-clathrate hydrate of TBAB, even at low molar fraction of CO<sub>2</sub>. However, it is observed a difference between the data of this work and the results of Duc *et al.*, (2007). The data from Duc *et al.*, (2007) has been determined with a liquid solution at TBAB mass fraction of 0.4. In our work, the TBAB mass fraction is in the range [0.07-0.18] and could explain the difference. But independently of the differences, it can be underlined that the semi-clathrate hydrate of TBAB has a better affinity to CO<sub>2</sub> in comparison to pure water clathrate hydrate.

For example, at a gas molar fraction of CO<sub>2</sub> around 0.2, the CO<sub>2</sub> molar fraction in the clathrate hydrate is in the range of 0.43 (T=288.15K) to 0.42 (T=283.15K) whereas the CO<sub>2</sub> molar fraction in the TBAB semi-clathrate hydrate can be up to 0.93 (from Duc *et al.*, (2007) at a temperature of 286.15K).

Similarly, at gas molar fraction of CO<sub>2</sub> around the value of 0.5, the CO<sub>2</sub> molar fraction in the clathrate hydrate is in the range 0.66 (T=288.15) to 0.79 (T=283.15) whereas the CO<sub>2</sub> molar fraction in the TBAB semi-clathrate hydrate can be up to 0.96 (Herri et al, 2014) at a temperature of 285.5K).

Brantuas (2013) has also reported the Gas Storage Capacity of some quaternary ammonium salts. The first experimental fact is the low value in the range of [30-60 m<sup>3</sup>/m<sup>3</sup>], but also that there is no clear relationship in between the pressure and the Gas Storage Capacity.

**Table 1** CO<sub>2</sub> Gas Storage Capacity of Quaternary Ammonium Salts (From Brantuas, 2013)

Experiment	CO <sub>2</sub> pressure (bars)	Gas Storage Capacity (m <sup>3</sup> /m <sup>3</sup> )
TBAB	8.5	33.6
TBPB (experiment 1)	6.3	30.6
TBPB (experiment 2)	7.9	57.0
TBPB (experiment 3)	4.9	61.4
TBACl (experiment 1)	13.8	39.4
TBACl (experiment 2)	10.1	23.5
TBACl (experiment 3)	8.1	44.7
TBACl (experiment 4)	7.8	45.7
TBACl (experiment 5)	8.3	45.4
TBAF	13.6	45.3

## CONCLUSIONS

The main conclusions regarding the benefits and drawbacks of thermodynamic additives can be summarized as follows:

- the operating temperature cannot be lower than the temperature of formation of the pure promoter hydrate, for example 281K for Cyclopentane, or 285K for the TBAB. At lower temperature, there is a competition between the pure promoter hydrate, and the mix gas promoter hydrate which affects the Gas Storage Capacity of the hydrate phase,
- the selectivity of the CO<sub>2</sub> separation is slightly enhanced in presence of CP, and very slightly enhanced in presence of TBAB,
- the equilibrium pressure depends on the difference of temperature  $\Delta T$  between the operating temperature and the temperature of formation of the pure promoter hydrate,
- the equilibrium pressure tends to 0 as  $\Delta T$  tends to 0,
- the storage capacity is low. From a theoretical point of view (see paper 2 in this series of 4 papers), the storage capacity vanishes as the pressure tends to 0.

So, there is a fundamental contradiction between the benefits of a thermodynamic additive to drop the operating pressure, and the drawback in terms of gas storage capacity which decreases, as the pressure drops.

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