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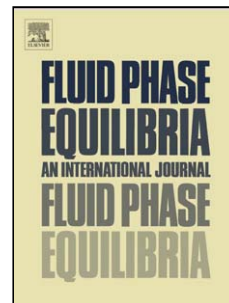
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# Phase equilibrium and dissociation enthalpy for semi-clathrate hydrate of CO<sub>2</sub>+TBAB

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## Abstract

The present work investigates equilibrium conditions and dissociation enthalpy of hydrates formed from CO<sub>2</sub>-TBAB(tetra-*n*-butylammonium bromide)-water mixtures. Differential Thermal Analysis (DTA) was used for Hydrate-Liquid-Vapour (H-L-V) equilibrium condition determination in a TBAB concentration range from 4.43 to 9.01 wt% and in a CO<sub>2</sub> pressure range from 0.3 to 2.5 MPa. The results showed that the presence of TBAB allowed decreasing the formation pressure of CO<sub>2</sub> hydrate by approximately 74 and 87% at 283 and 279 K, respectively. Moreover, pressure reductions were dependent on the TBAB concentration. The dissociation enthalpy and the composition of double hydrate formed from 9.01 wt% TBAB solution were determined by both the DTA and Clapeyron equation. The DTA method resulted in 313.2 kJ per kg of hydrate for the dissociation enthalpy and 2.51CO<sub>2</sub>·TBAB·38H<sub>2</sub>O for composition of the double hydrate. For the use of Clapeyron equation, the volume change was defined by taking into account the gas solubility in the liquid phase. The calculation results showed a discrepancy with the experimental data obtained by DTA, suggesting the limited application of Clapeyron equation in the CO<sub>2</sub>-TBAB-water system.

**Keywords:** Hydrate; CO<sub>2</sub>; Tetra-*n*-butylammonium bromide; Equilibrium; Dissociation enthalpy

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## 1. Introduction

With the enforcement of the Montreal and Kyoto Protocols, the primary refrigerants such as CFCs and HCFCs are phased out gradually from the refrigeration industry, due to their global warming and ozone depletion potentials. As a result, the interests for environment-friendly refrigerants increased considerably. CO<sub>2</sub> is one of the most harmless refrigerants except for water and air. Besides, CO<sub>2</sub> has the advantage of being non-toxic and is easily available [1]. Currently, various researches in the air-conditioning and heat pump field are devoted to the investigation of pure CO<sub>2</sub> as a primary refrigerant [2]. Despite the progress made on these researches, some parallel paths including the use of secondary refrigeration loops deserve to be explored.

Secondary refrigeration is capable of reducing the amount and the risk of leakage of primary refrigerants. Currently, ice slurries are used as secondary refrigerant, but their generators are power-limited because they use mechanical technologies (scraped or brushed-surface heat exchangers). Tetra-*n*-butylammonium bromide (TBAB) hydrate slurries were also studied in previous work [3-5]. Rigorously, TBAB and water form semi-clathrate hydrates. In these hydrates, some cages are broken to encage big guest species such as TBAB, and water molecules of the structure are partially replaced by the atoms of guest species [6]. TBAB hydrate slurries were studied due to their potential suitability for air-conditioning applications (stable between 273 and 285 K). Nevertheless, the generation of TBAB hydrate slurries could have the same drawbacks as ice slurries related to the use of mechanical generators. Moreover, the dissociation enthalpy of TBAB hydrate ( $\sim 200 \text{ kJ}\cdot\text{kg}^{-1}$ ) [7] is lower than that of ice ( $333 \text{ kJ}\cdot\text{kg}^{-1}$ ).

CO<sub>2</sub> hydrate slurry is well suited for use as secondary refrigerant, since it can be generated by CO<sub>2</sub> injection in a cold aqueous solution (non-mechanical process) and it has a large thermal storage capacity thanks to the large dissociation enthalpy of CO<sub>2</sub> hydrate. In addition, some hydrate slurries are non-cohesive, so that they can flow steadily through piping systems and heat exchangers without coagulating [4]. The CO<sub>2</sub> hydrate dissociation enthalpy was investigated by many researchers based on experimental or calculation methods [8-10]. The results showed that the dissociation enthalpy of CO<sub>2</sub> hydrate ( $374 \text{ kJ}\cdot\text{kg}^{-1}$ ) was higher than that of ice, which has higher thermal storage capacity than most of traditional materials used in refrigeration. However, the CO<sub>2</sub>-hydrate formation pressure is higher than that required in cooling systems such as air-conditioning (approx.  $< 1 \text{ MPa}$ ). Therefore, another component needs to be added to reduce the

CO<sub>2</sub>-hydrate formation pressure. Previous researches showed that the presence of tetrahydrofuran (THF) in water could reduce the formation pressure of CO<sub>2</sub> hydrate significantly [11].

In the present work, TBAB was used to reduce the formation pressure of CO<sub>2</sub> hydrate because it could form hydrate at atmospheric pressure, and so was likely to form a double hydrate with CO<sub>2</sub> at a lower pressure than that of single CO<sub>2</sub> hydrate. The equilibrium conditions and the dissociation enthalpy of (CO<sub>2</sub>+TBAB) double hydrates were studied by Differential Thermal Analysis (DTA) and also calculated by the Clapeyron equation. The CO<sub>2</sub> pressure range was from 0.3 to 2.5 MPa. The TBAB concentration range was from 4.43 to 9.01 wt%. Low TBAB concentrations were chosen in order to reduce the amount of TBAB in the case of environment-friendly refrigeration applications.

One of the objectives of this work is to show that the formation pressures of (CO<sub>2</sub>+TBAB) hydrates are sufficiently low to be suitable for refrigeration application conditions. Moreover, the dissociation enthalpy of (CO<sub>2</sub>+TBAB) hydrates has to be sufficiently high. Finally, (CO<sub>2</sub>+TBAB) hydrates have to be stable at higher temperature than TBAB hydrate in order to be formed by CO<sub>2</sub> injection in a cold TBAB-water solution (non-mechanical process).

## 2. Experimental

### 2.1. Apparatus and materials

All the measurements were performed using DTA equipment, which was described in detail in a previous work [9]. The DTA device (Fig. 1) consisted of two symmetric transparent glass cells (inner diameter of 30 mm; volume of 46 cm<sup>3</sup>) equipped with a magnetic stirrer and immersed in a temperature-controlled bath. The two cells were filled with TBAB aqueous solution and inert solution, respectively. A T-type thermocouple ( $\pm 0.3$  K) was placed inside each cell, and two pressure gauges (0-4 MPa,  $\pm 0.05\%$  full scale) were used to measure the “in situ” fluid pressure. Another eight T-type thermocouples were connected in series to measure the temperature difference between the two cells. This temperature difference was then converted into a DTA signal (mV). A syringe pump was equipped for quantifying the amount of injected CO<sub>2</sub>. HPLC grade TBAB (purity > 99 %, Fisher Scientific) and deionized water were used to prepare all the solutions.

## 2.2. Protocol

### 2.2.1. Solubility of CO<sub>2</sub> in TBAB solution

The solubility of CO<sub>2</sub> in the TBAB solution was measured as follows: an amount of TBAB solution was introduced into the sample cell at 293.1 K. The sample cell was evacuated to remove the air, and then pressurized by CO<sub>2</sub> injection. The stirrer was used to accelerate the gas dissolution, resulting in a pressure decrease. When the CO<sub>2</sub> dissolution equilibrium was reached, pressure and temperature were recorded, and then temperature was changed to measure another condition. This protocol was applied for various pressures and temperatures. The mole fraction of CO<sub>2</sub> in TBAB solution could be calculated by Eq. (1):

$$x_{\text{CO}_2} = \frac{n_{\text{CO}_2}^{\text{L}}}{n_{\text{CO}_2}^{\text{L}} + n_{\text{TBAB}}^{\text{L}} + n_{\text{w}}^{\text{L}}} \quad (1)$$

where  $n_{\text{TBAB}}^{\text{L}}$  and  $n_{\text{w}}^{\text{L}}$  are the number of moles of TBAB and water in liquid phase, respectively.

The quantity of CO<sub>2</sub> in the liquid phase  $n_{\text{CO}_2}^{\text{L}}$  is given by:

$$n_{\text{CO}_2}^{\text{L}} = n_{\text{CO}_2}^{\text{tot}} - \frac{PV_{\text{CO}_2}}{ZRT} \quad (2)$$

where  $n_{\text{CO}_2}^{\text{tot}}$  is the total number of moles of CO<sub>2</sub> in the system, which was determined using the syringe pump.

### 2.2.2. Differential thermal analysis

The system was cooled slowly (about 0.14 K·min<sup>-1</sup>) with agitation to 268.1 K in order to crystallize the sample. A marked pressure drop (accompanied by a temperature increase) indicated the exothermic formation of hydrates. Once all the liquid was converted into solids and the pressure of the system reached a steady state, the bath temperature was increased to melt the solids with a heating rate of 0.07 K·min<sup>-1</sup>. The melting points were determined following two methods. For congruent melting, such as at a eutectic point, the phase-change pressure and temperature corresponded to the extrapolated onset of the DTA curve. For incongruent melting, e.g. of the (CO<sub>2</sub>+TBAB) double hydrate, progressive endothermic peak appeared during the

heating process. The phase-change pressure and temperature corresponded to the end of the last DTA peak. The measurements were performed at several initial pressures and then a hydrate-liquid-vapour equilibrium curve was obtained. At least 2 parallel runs were conducted to guarantee the accuracy of the experimental data.

### 3. Equilibrium results and discussion

#### 3.1. DTA experiments for the TBAB-water system

Before studying the CO<sub>2</sub>-TBAB-water system, the melting points of solids formed in the TBAB-water system in a TBAB concentration range from 4.43 to 9.01 wt% were measured and compared with literature data. Fig. 2 shows the phase diagram of TBAB hydrates at atmospheric pressure. There are two types of TBAB hydrate termed type A and B having different melting temperatures. However, at a given concentration, only the phase-change temperature of the stable TBAB hydrate could be determined. As shown in Fig. 2, type B TBAB hydrate was more stable than type A hydrate in the TBAB concentration range from 4.43 to 9.01 wt%. Table 1 lists the phase-change temperatures of the eutectic mixtures and type B TBAB hydrate. It was observed that our data were in good agreement with those presented by Oyama et al. [7].

#### 3.2. Experiments for the CO<sub>2</sub>-TBAB-water system

##### 3.2.1. CO<sub>2</sub> solubility in the TBAB solutions

Fig. 3 shows the CO<sub>2</sub> solubility (in mole fraction) in TBAB solutions for various TBAB concentrations (range from 4.43 to 10 wt%) as a function of pressure. Fig. 3 also shows literature data related to the CO<sub>2</sub> solubility in pure water [12, 13]. The CO<sub>2</sub> solubility in TBAB solution was slightly lower than that in pure water. This difference became larger at higher pressure. The solubility points also showed that the TBAB concentration had no significant effect on the CO<sub>2</sub> solubility in the TBAB concentration range from 4.43 to 10 wt% and in the pressure range from 0.5 to 1.6 MPa. Kamata et al. [14] reported that the CO<sub>2</sub> solubility in 10 wt% TBAB solution at atmospheric pressure was almost equal to that in pure water.

### 3.2.2. Solid components in the $\text{CO}_2$ -TBAB-water system

Fig. 4 shows DTA and pressure curves in the heating process for the solids formed in the  $\text{CO}_2$ -TBAB-water system. The initial conditions were 9.01 wt% for TBAB concentration, 2 MPa for pressure and 293.15 K for temperature. The first endothermic peak was due to the dissociation of the eutectic mixture. The eutectic mixture comprised type A TBAB hydrate (or double hydrate) and ice (or  $\text{CO}_2$  hydrate), since type B hydrate has no eutectic point [7]. During the eutectic melting, the pressure decreased firstly as consequence of gas volume increase as well as gas dissolution in the released liquid phase, and then it remained constant. The constant pressure suggested that only  $\text{CO}_2$ -free solids (type A TBAB hydrate and ice) were contained in the eutectic mixture. Moreover, if  $\text{CO}_2$ -containing hydrate existed in the eutectic mixture, an increase in initial pressure should lead to an increase in the congruent melting temperature. On the contrary, the experimental result showed that congruent melting temperature decreased from 272.8 to 271.8 K when the initial pressure increased from 0.5 to 2 MPa. This phenomenon was ascribed to the fact that the increase of the  $\text{CO}_2$  amount in the liquid phase reduced the freezing point of water.

In Fig. 4, the following two peaks were considered to correspond to type A and B ( $\text{CO}_2$ +TBAB) double hydrates, as  $\text{CO}_2$  was released, resulting in a pressure increase. According to the phase diagram of TBAB hydrates, we deduced that type B ( $\text{CO}_2$ +TBAB) double hydrates are more stable than type A in a TBAB concentration range from eutectic point to 19 wt%. Therefore, the second and third endothermic peaks were due to type A and type B double hydrate, respectively. The pressure curve exhibited an inflection point, after which the pressure increased linearly with time. The pressure and temperature corresponding to the inflection point were the equilibrium conditions of the double hydrate. It was noted that all the equilibrium  $P$ - $T$  data determined in this work were for type B double hydrate.

### 3.3. Equilibrium condition for $\text{CO}_2$ +TBAB double hydrate

Three-phase (H-L-V) equilibrium conditions for the  $\text{CO}_2$ -TBAB-water system were not reported by other researchers except for Duc et al. [15]. Fig. 5 shows the experimental  $P$ - $T$  data for the  $\text{CO}_2$ -TBAB-water system determined by both Duc et al. [15] and in this work. It was observed that part of the data of Duc et al. [15] were consistent with our data. For example, at 279.4 K, the measured formation pressure at a TBAB concentration of 4.43 wt% (present work)



was quite similar to that at 4.96 wt% obtained by Duc et al. [15]. In addition, two points from Duc et al. [15] for a TBAB concentration of 9.91 wt% were close to our curve at 9.01 wt%. However, an important feature of the study of Duc et al. [15] was related to their claim that the TBAB concentration did not have a significant influence on the hydrate formation pressure in the TBAB concentration range from 4.96 to 65.04 wt%. The reason was that the equilibrium pressures of (CO<sub>2</sub>+TBAB) hydrate at 284 K in the two cases of TBAB concentrations of 4.96 and 65.04 wt% were very close, i.e. 0.84 and 0.815 MPa, respectively. Furthermore, for the points at 4.96, 9.91 and 65.04 wt%, the pressure just increased with temperature no matter what the concentration was. On the contrary, our results showed the following characteristics: the formation pressure of double hydrate was dependent on the concentration of TBAB between 4.43 and 9.01 wt%. Moreover, our work showed that the higher the TBAB concentration was, the lower the hydrate formation pressure was. Based on our results, we had a suspicion against remarks and results of Duc et al. [15]. Complementary analyses based on literature data are specified in the subsequent section.

Jager et al. [16] found that in the CH<sub>4</sub>+1,4-dioxane+water system, the equilibrium pressure of the hydrate showed a minimum at a concentration of 6 mol%, around the stoichiometric ratio of the soluble hydrate former and water (ratio of large sII cages to water). Based on their observation, we believed that, at a given temperature, the equilibrium pressure of (CO<sub>2</sub>+TBAB) double hydrates was lowest when TBAB concentration was stoichiometric, i.e. 40 and 32 wt% for type A and B hydrates, respectively, as shown in Fig. 2 [7]. This could be responsible for the closeness of equilibrium pressure for TBAB concentration at 4.96 and 65.04 wt% at 284 K in the work of Duc et al. [15].

On the other hand, for each concentration, only two or three points were measured by Duc et al. [15], which was not sufficient to illustrate clearly the influence of TBAB concentration on the equilibrium pressure. In addition, the type of double hydrate in the experimental results of Duc et al. [15] was not specified. In our opinions, the points for TBAB concentration of 4.96 and 9.91 wt% should be for type B double hydrate, while the points at 40.11 wt% should be for type A double hydrate, because type A hydrate was more stable than type B between 19 to 45 wt%.

The experimental data of three-phase (H-L-V) equilibria for type B double hydrate are presented in Table 2 and plotted in Fig. 6. This figure also shows the equilibrium data of

CO<sub>2</sub> hydrate and (CO<sub>2</sub>+THF) hydrate for comparison [11, 17]. From Fig. 6, a substantial decrease in CO<sub>2</sub>-hydrate formation pressure was observed in the presence of TBAB. The pressure was reduced from 3.495 to 0.763 MPa at 281.46 K when 4.43 wt% of TBAB was added in the aqueous solution.

Fig. 6 also showed that the reduction of CO<sub>2</sub>-hydrate formation pressure caused by TBAB addition was close to that caused by THF addition. This pressure reduction was approximately 80 %. However, the formation pressure of (CO<sub>2</sub>+TBAB) double hydrate showed a stronger dependency on temperature than that of (CO<sub>2</sub>+THF) hydrate. For example, the formation pressure of (CO<sub>2</sub>+TBAB) (9.01 wt %) hydrate increased from 0.391 to 2.274 MPa between 282.79 and 288.09 K, whereas the formation pressure for (CO<sub>2</sub>+THF) (10.16 wt%) hydrate increased from 0.507 to 1.655 MPa. Although the addition of a small amount of TBAB into water expanded the hydrate stability region, TBAB could have an inhibiting effect at certain composition or temperature conditions. Imai et al. [18] reported that in the (HFC-32+TBAB(43 wt%)+water) system, TBAB changed from thermodynamic promoter to inhibitor for hydrate formation at 289.4 K.

#### 4. Dissociation enthalpy results and discussion

Dissociation enthalpies of gas hydrates are usually obtained by two methods: direct calorimetric determination and indirect calculation using the Clapeyron or Clausius-Clapeyron equation and equilibrium *P-T* data. In this study, the dissociation enthalpy of (CO<sub>2</sub>+TBAB) double hydrate was determined by DTA, and the results were compared to those calculated by the Clapeyron equation. According to Davidson [6], TBAB semi-clathrate hydrate is stoichiometric, in contrast to gas hydrates. Moreover, no structural transition occurred when CO<sub>2</sub> was encaged in the semi-clathrate [19]. Consequently, the compositions of TBAB and water in the double hydrate were the same as those in the single TBAB hydrate, whereas the composition of CO<sub>2</sub> was unknown. Here, the formula of type B double hydrate was described by  $a\text{CO}_2 \cdot \text{TBAB} \cdot 38\text{H}_2\text{O}$ . Hereinafter, for simplicity, double hydrate referred to type B (CO<sub>2</sub>+TBAB) hydrate unless otherwise stated.

##### 4.1. Calorimetric method

In order to determine the dissociation enthalpy of double hydrate, the quantity of double hydrate and the heat absorbed during its dissociation had to be accurately measured. As mentioned previously, the third endothermic peak in Fig. 4 represented the dissociation of double hydrate; the amount of absorbed heat could be obtained by integrating the DTA signal (calibrated with ice) with time.

#### 4.1.1. Quantity of double hydrate $n_{DH}$

After the entire sample crystallized, the solids obtained were the eutectic mixture (type A TBAB hydrate and ice), type A double hydrate and type B double hydrate. From Fig. 4, it was noticed that the peak area of type A double hydrate was considerably smaller than that of type B double hydrate and eutectic, implying the quantity of type A double hydrate in the solids can be neglected. If one assumed that before melting, the solids were only type B double hydrate and eutectic mixture (type A TBAB hydrate and ice), the lever principle could allow us to calculate the masses of TBAB contained in type B double hydrate and type A TBAB hydrate, and also the mass of ice in the eutectic mixture. Then, various mass fractions could be calculated by the following equation set:

$$\begin{aligned} w_{TBAB}^B &= \frac{(w_0 - w_E)}{(1 - w_E / w_S^B)} \\ w_{TBAB}^A &= \frac{w_E (w_S^B - w_0)}{w_S^B - w_E} \\ w_{ICE} &= \frac{(w_S^A - w_E)(w_S^B - w_0)}{(w_S^B - w_E)w_S^A} \end{aligned} \quad (3)$$

where  $w_{TBAB}^B$  is the mass fraction expressing the mass of TBAB in type B double hydrate divided by the total mass of TBAB and water in the system;  $w_{TBAB}^A$  is the mass fraction expressing the mass of TBAB in type A TBAB hydrate divided by the total mass of TBAB and water in the system;  $w_{ICE}$  is the mass fraction expressing the mass of ice in the eutectic mixture divided by the total mass of TBAB and water in the system;  $w_S^A$  and  $w_S^B$  are the stoichiometric mass fractions of

TBAB in type A and B TBAB hydrate, respectively;  $w_E$  is the eutectic mass fraction of TBAB in the TBAB-water system;  $w_0$  is the total TBAB mass fraction in the system at initial state.

From Equation set (3), the number of moles of double hydrate  $n_{DH}$ , which is the same as that of TBAB in the double hydrate  $n_{TBAB}^{DH}$ , could be calculated as follows:

$$n_{DH} = n_{TBAB}^{DH} = \frac{w_{TBAB}^B \times (m_{TBAB}^{tot} + m_w^{tot})}{M_{TBAB}} \quad (4)$$

where  $m_{TBAB}^{tot}$  and  $m_w^{tot}$  are the total mass of TBAB and water in the system, respectively;  $M_{TBAB}$  is molecular weight of TBAB.

#### 4.1.2. Quantity of $CO_2$ in double hydrate $n_{CO_2}^{DH}$

After the eutectic mixture melted, the system was composed of TBAB liquid solution (at eutectic concentration) saturated with  $CO_2$ , double hydrate and vapour. The  $CO_2$  quantity in the double hydrate  $n_{CO_2}^{DH}$  could be calculated from  $PVT$  data and the  $CO_2$  solubility in the TBAB solution, as shown in Eq. (5).

$$n_{CO_2}^{DH} = n_{CO_2}^{tot} - \frac{PV_{CO_2}}{ZRT} - \frac{x_{CO_2}}{1 - x_{CO_2}} (n_{TBAB}^L + n_w^L) \quad (5)$$

where  $P$  and  $T$  are the pressure and temperature corresponding to the onset of the DTA peak of the double hydrate;  $n_{TBAB}^L$  and  $n_w^L$  are the number of moles of TBAB and water in the liquid phase, respectively. They could be obtained from Eq. (3). The gas volume  $V_{CO_2}$  is given by:

$$V_{CO_2} = V^{tot} - \frac{M_{TBAB} n_{TBAB}^L + M_w n_w^L}{\rho_{w, TBAB}} - n_{DH} v_{DH} \quad (6)$$

where  $V^{tot}$  is the total volume of the system;  $v_{DH}$  is the molar volume of the double hydrate. Obata et al. [4] reported that the density of type B hydrate (TBAB·38H<sub>2</sub>O) was 1030 kg·m<sup>-3</sup>, corresponding to 9.77e<sup>-4</sup> m<sup>3</sup>·mol<sup>-1</sup>, which approximated that of double hydrate ( $\alpha CO_2$ ·TBAB·38H<sub>2</sub>O). Finally, the density of TBAB solution  $\rho_{w, TBAB}$  at different temperatures was available from Duc et al. [15].

#### 4.1.3. Composition of double hydrate

Eq. (4) and Eq. (5) allowed us to calculate the composition of CO<sub>2</sub> in the double hydrate, noted  $a$ . Table 3 lists the results of dissociation enthalpy and composition of the double hydrate. The initial conditions of the sample were 9.01 wt% for TBAB concentration, 2 MPa for pressure and 293.15 K for temperature. The dissociation enthalpy of double hydrate was expressed as both per mass of hydrate and per mole of CO<sub>2</sub>. From Table 3, the value of  $\Delta H_d$  of double hydrate expressed in kJ per mass of hydrate was lower than that of CO<sub>2</sub> hydrate but was close to that of ice. On the other hand, the value of  $\Delta H_d$  of double hydrate expressed in kJ per mole of CO<sub>2</sub> was higher than that of CO<sub>2</sub> hydrate. The composition of double hydrate was evaluated to be 2.51CO<sub>2</sub>·TBAB·38H<sub>2</sub>O. We can note that the maximal value of  $a$  is 3 [20], corresponding to a fractional occupancy of dodecahedral cages with CO<sub>2</sub> molecule of 84%.

#### 4.2. Clapeyron equation

Previous work pointed out that the Clapeyron equation could be used to calculate the dissociation enthalpy of gas hydrate as long as the system was univariant, as in the case of simple hydrates [21]. In the present work, the CO<sub>2</sub>-TBAB-water system is not monovariant. However, other authors used Clausius-Clapeyron equation for systems which were not monovariant such as the CH<sub>4</sub>-C<sub>2</sub>H<sub>6</sub>-water system [17, 22]. Considering that DTA results have to be compared to results obtained by another method, the Clapeyron equation is used as in previous work to calculate in a first approach the dissociation enthalpy of the double hydrate.

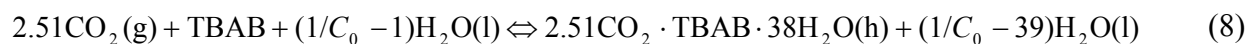
##### 4.2.1. Theory analysis

When (CO<sub>2</sub>+TBAB) double hydrate is formed from the TBAB solution at stoichiometric concentration, all the water is converted into hydrate. Based on the formula of double hydrate evaluated in paragraph 4.1.3, the double-hydrate formation process can be written as:



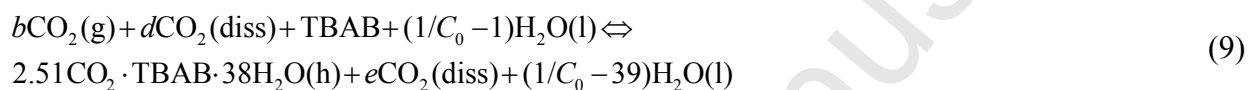
When the mass fraction of TBAB is lower than the stoichiometric concentration (32 wt%), the water content exceeds the quantity needed to form double hydrate, suggesting that excess water is

also in equilibrium with double hydrate. In this case, the formation of double hydrate from gaseous CO<sub>2</sub> and TBAB solution can be expressed by Eq. (8):



where  $C_0$  is the initial molar fraction of TBAB in the liquid phase.

However, Eq. (8) corresponds to an ideal state. In fact, the real state is that part of CO<sub>2</sub> in the vapour phase is dissolved in the liquid phase. Eq. (9) describes the real formation process for double hydrate, where "diss" relates to CO<sub>2</sub> dissolved in the liquid phase at equilibrium pressure and temperature.



#### 4.2.2. Determination of $\Delta H_d$ using Clapeyron equation

In the presence of excess water, according to Eq. (9), the dissociation enthalpy of double hydrate is calculated by the Clapeyron equation in the following form:

$$\frac{dP}{dT} = \frac{\Delta H_f}{T\Delta V} \quad (10)$$

The total volume change  $\Delta V$  related to Eqs. (9) and (10) was calculated based on Anderson's work [8], as follows:

$$\Delta V = V_{\text{DH}} + V_{\text{w,CO}_2} - bv_{\text{CO}_2}^{\text{v}} - V_{\text{w,TBAB,CO}_2} \quad (11)$$

where  $v_{\text{CO}_2}^{\text{v}}$  denotes the molar volume of CO<sub>2</sub> in the vapour phase at  $T$  and  $P$ ;  $V_{\text{w,CO}_2}$  and  $V_{\text{w,TBAB,CO}_2}$  are the volume of the water and aqueous TBAB saturated with CO<sub>2</sub>, respectively; the coefficient  $b$  is given by the following equation based on the mass balance of CO<sub>2</sub> in Eq. (9):

$$b = 2.51 + e - d \quad (12)$$

where  $d$  and  $e$  are the number of moles of CO<sub>2</sub> dissolved at  $T$  and  $P$  in the TBAB solution and pure water, respectively. These values could be determined using the measured CO<sub>2</sub> solubility in TBAB solution as well as in water (literature data).

The liquid phase volumes  $V_{w,CO_2}$  and  $V_{w,TBAB,CO_2}$  can be calculated by Eq. (13) and (14), respectively:

$$V_{w,CO_2} = e \times v_{CO_2}^L + (1/C_0 - 39) \times v_w \quad (13)$$

$$V_{w,TBAB,CO_2} = d \times v_{CO_2}^L + \frac{M_{TBAB} + (1/C_0 - 1)M_w}{\rho_{w,TBAB}} \quad (14)$$

where  $v_{CO_2}^L$  is the partial molar volume of  $CO_2$  in liquid phase, which is assumed to be the partial molar volume of  $CO_2$  in pure water, i.e.  $3.84e^{-5} \text{ m}^3 \cdot \text{mol}^{-1}$  [8].  $v_w$  is the molar volume of water.

The results for the dissociation enthalpy of ( $CO_2$ +TBAB) double hydrate are given in Table 4. In addition, dissociation enthalpies related to other  $CO_2$  containing mixtures as  $CO_2$ -THF-water and  $CO_2$ - $N_2$ -THF-water systems are listed in Table 4.

#### 4.3. Comparison between calorimetric and Clapeyron equation results

In this study, no experimental data obtained by DTA is available at a TBAB concentration of 4.43 wt%, because the endothermic peaks of eutectic and double hydrate are overlapping seriously. For 9.01 wt% TBAB solution,  $\Delta H_d$  obtained from the Clapeyron equation at 282.8 K was found to be about 45 % higher than the value measured by DTA (Table 4). This discrepancy can be explained by the following arguments:

(1) The TBAB concentration has an evident effect on the dissociation enthalpy of the double hydrate between 4.43 and 9.01 wt%, as shown by the results from the Clapeyron equation in Table 4. This behaviour was previously observed with THF-containing hydrates [23]. However, in the case of DTA experiments, the TBAB concentration varied from the eutectic point to the initial state (9.01 wt%) during the melting of double hydrate. This can partly explain the discrepancy between DTA results and results based on the Clapeyron equation at constant TBAB concentration.

(2) Another argument could be related to the accuracy of equilibrium curve. This possibility might lead to uncertainties of the dissociation enthalpy obtained from the Clapeyron equation. For instance, if the equilibrium temperature corresponding to 0.391 MPa is shifted from 282.8 to 282.5 K, the dissociation enthalpy of hydrate would decrease by about 8%.

(3) It is proposed that 80% of the hydrate dissociation enthalpy is due to the strength of water hydrogen bonds in the hydrate structure [22]. The hydrate dissociation enthalpy is thus strongly related to the hydration number. Consequently, the ratio between the hydration numbers of CO<sub>2</sub> hydrate (7.23) and (CO<sub>2</sub>+TBAB) hydrates (38/2.51=15.1) should be close to the ratio between the dissociation enthalpies of CO<sub>2</sub> and (CO<sub>2</sub>+TBAB) hydrates (Table 4). This assumption is confirmed in the case of calorimetric data but not in the case of the Clapeyron equation results.

(4) Finally, the analysis based on the use of Clapeyron equation may be not completely appropriate to our system. This analysis includes the assumption related to monovariant systems (introduction of part 4.2) and the definition of volume change.

## 5. Conclusions

The three phase (H-L-V) equilibrium conditions of hydrates formed in the CO<sub>2</sub>-TBAB-water system were investigated in this work by using a DTA device in a TBAB concentration range from 4.43 to 9.01 wt% and in a CO<sub>2</sub> pressure range from 0.3 to 2.5 MPa. The results showed that the addition of TBAB reduced the formation pressures of CO<sub>2</sub> hydrate by approximately 80%. This leads to values below 1 MPa in the temperature range of 279 – 285 K, which fulfilled the requirement of air-conditioning system. Moreover, a higher concentration of TBAB led to higher pressure reduction of the double hydrate.

Based on the solids formed from a 9 wt% TBAB solution at 2 MPa CO<sub>2</sub> pressure, the dissociation enthalpy of CO<sub>2</sub>+TBAB double hydrate measured by DTA was 313.2 kJ per kg double hydrate, lower than that of CO<sub>2</sub> hydrate but close to that of ice. In addition, DTA results showed that the composition of double hydrate was 2.51CO<sub>2</sub>·TBAB·38H<sub>2</sub>O. The fractional occupancy of dodecahedral cages by CO<sub>2</sub> in the semi-clathrate hydrate was thus deduced to be 84%.

The incongruent formation process of double hydrate was described for an initial TBAB concentration lower than the stoichiometric value. The dissociation enthalpy of (CO<sub>2</sub>+TBAB) double hydrate was calculated using the Clapeyron equation based on equilibrium *P-T* data measured by DTA for TBAB concentrations of 4.43 and 9.01 wt%. The CO<sub>2</sub> dissolution in the liquid phase is taken into account. The calculated value at 9.01 wt% appeared to be notably different from the experimental data. The latter is however preferably accepted based on various



arguments against the application of Clapeyron equation in our case such as non-monovariant system and differentiation accuracy. In order to check the enthalpy results, the differential scanning calorimetry (DSC) method will be used to measure the dissociation enthalpy of CO<sub>2</sub>+TBAB double hydrate in a further work. Moreover, the definitions related to the use of Clapeyron equation in our system could be improved.

## Nomenclature

$a$	molar ratio of CO <sub>2</sub> to TBAB in type B double hydrate
$C_0$	initial molar fraction of TBAB in the solution
H-L-V	hydrate-liquid-vapour
$M$	molecular weight (kg·mol <sup>-1</sup> )
$m$	mass (kg)
$nb_h$	hydration number
$n_i$	number of moles of component $i$ (mol)
$P$	pressure (Pa)
$R$	universal gas constant (J·mol <sup>-1</sup> ·K <sup>-1</sup> )
$T$	absolute temperature (K)
$v$	molar volume (m <sup>3</sup> ·mol <sup>-1</sup> )
$V$	volume (m <sup>3</sup> )
$x_{CO_2}$	molar fraction of CO <sub>2</sub> in TBAB solution
$w_0$	mass fraction of TBAB in the liquid phase at initial state
$w_E$	mass fraction of TBAB in the liquid phase at eutectic state
$w_{ICE}$	mass of ice in eutectic mixture divided by the total mass of TBAB and water in the system
$w_S^A$	stoichiometric mass fraction of TBAB in type A TBAB hydrate
$w_S^B$	stoichiometric mass fraction of TBAB in type B TBAB hydrate
$w_{TBAB}^A$	mass of TBAB in eutectic mixture divided by total mass of TBAB and water in the system
$w_{TBAB}^B$	mass of TBAB in type B double hydrate divided by total mass of TBAB and water in the system
$Z$	gas compressibility factor

## Greek symbol

$\rho$	density (kg·m <sup>-3</sup> )
$\Delta H_d$	dissociation enthalpy (kJ·mol <sup>-1</sup> ) or (kJ·kg <sup>-1</sup> )

$\Delta H_f$  formation enthalpy ( $\text{kJ}\cdot\text{mol}^{-1}$ ) or ( $\text{kJ}\cdot\text{kg}^{-1}$ )

***Superscripts***

DH double hydrate phase

L liquid phase

tot total

V vapour phase

***Subscripts***

DH double hydrate

w water

w, CO<sub>2</sub> water saturated with CO<sub>2</sub>

w, TBAB TBAB solution

w, TBAB, CO<sub>2</sub> TBAB solution saturated with CO<sub>2</sub>

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## Caption of tables and figures

Table 1 Phase-change temperatures for the solids in TBAB-water system

Table 2 Three-phase (H-L-V) equilibrium conditions for CO<sub>2</sub>+TBAB double hydrate at different TBAB concentrations

Table 3 Comparison of dissociation enthalpies for ice and hydrates of  $\alpha$ -CO<sub>2</sub>·TBAB·38H<sub>2</sub>O, CO<sub>2</sub>·nb<sub>h</sub>H<sub>2</sub>O

Table 4 Measured and reported dissociation enthalpies of different hydrates obtained by calorimetric method and Clapeyron / Clausius-Clapeyron equation

Fig. 1. Experimental DTA device: (1) sample cell; (2) reference cell; (3) temperature-controlled bath; (4) cooling/heating unit; (5) syringe pump; (6) CO<sub>2</sub> bottle; (7) acquisition interface; (8) thermocouples and differential thermal analysis; (9) pressure gauges.

Fig. 2. Phase diagram of TBAB hydrates at atmospheric pressure [7].

Fig. 3. Solubility of CO<sub>2</sub> in TBAB aqueous at 283.1 K.

Fig. 4. DTA and pressure profiles in heating for the solids formed from CO<sub>2</sub>-TBAB-water system (initial TBAB concentration: 9.01 wt%, initial CO<sub>2</sub> pressure: 2 MPa, initial temperature: 293.15 K).

Fig. 5. Equilibrium conditions of hydrates in CO<sub>2</sub>-TBAB-water system.

Fig. 6. Equilibrium conditions of CO<sub>2</sub> hydrate in various systems.

Table 1

TBAB (wt%)	Present work		Oyama [7]	
	$T_E$ (K)	$T_B$ (K)	$T_E$ (K)	$T_B$ (K)
4.43	273.0	277.0	272.6	276.3
7.02	272.8	278.2	272.6	278.0
9.01	272.8	279.7	272.6	279.3

$T_E$ : Eutectic temperature of type A simple hydrate and ice.

$T_B$ : melting temperature of type B simple hydrate.

Table 2

9.01		Mass fraction, TBAB (wt%)		4.43	
		7.02			
<i>T</i> (K)	<i>P</i> (MPa)	<i>T</i> (K)	<i>P</i> (MPa)	<i>T</i> (K)	<i>P</i> (MPa)
282.79	0.391	282.59	0.379	279.40	0.344
283.34	0.393	282.72	0.379	280.19	0.515
284.43	0.583	283.40	0.578	280.56	0.513
285.07	0.859	283.58	0.575	281.46	0.763
285.33	0.866	284.58	0.842	282.91	1.172
286.38	1.333	285.38	1.216	283.16	1.179
286.53	1.339	286.14	1.667	284.66	1.715
287.6	1.803	286.96	2.199		
288.09	2.274				

Average absolute deviation for pressure results (AADP%): 5%

Table 3

	$\Delta H_d$ (kJ·kg <sup>-1</sup> )	$\Delta H_d$ (kJ·mol <sup>-1</sup> <sub>CO<sub>2</sub></sub> )	Composition
CO <sub>2</sub> +TBAB double hydrate	313.2	139.5±9.85	$a=2.51$
CO <sub>2</sub> hydrate [23]	374.4	65.2±1.33	$nb_h=7.23$
Ice	333.3		

Table 4

Guests	Concentration of TBAB or THF(wt%)	$\Delta H_d$ (kJ · mol <sup>-1</sup> <sub>CO<sub>2</sub></sub> )	
		Calorimetry	Clapeyron
TBAB+CO <sub>2</sub>	4.43		168.2 <sup>a</sup>
	9.01	139.5±9.85	203.6 <sup>a</sup>
CO <sub>2</sub>	0	65.22±1.33 <sup>b</sup>	63.6 <sup>c</sup>
<sup>d</sup> THF+CO <sub>2</sub>	3.80		130
	10.16		147
<sup>b</sup> THF+CO <sub>2</sub> +N <sub>2</sub>	3.88	109.01±1.72	
	11.65	118.94±1.87	

<sup>a</sup>: Current work,  $T=282.8$  K.

<sup>b</sup>: Ref. [23],  $T=273.65$  K, for THF+CO<sub>2</sub>+N<sub>2</sub> gas composition is 17 mol%CO<sub>2</sub>+83 mol%N<sub>2</sub>.

<sup>c</sup>: Ref. [8],  $T=283.1$  K.

<sup>d</sup>: Ref. [11],  $T=280$  K, calculated with Clausius-Clapeyron equation.



Fig. 1

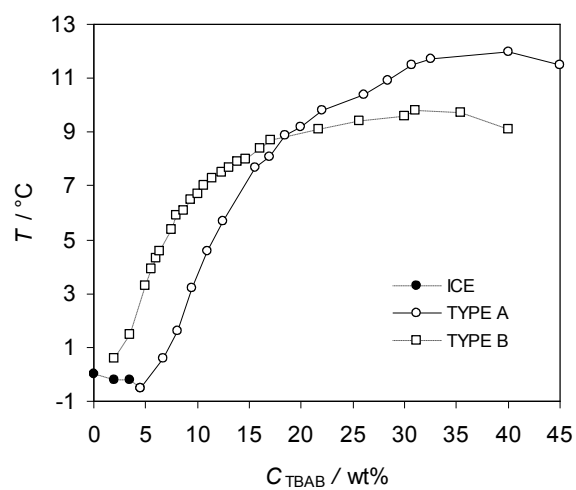


Fig. 2

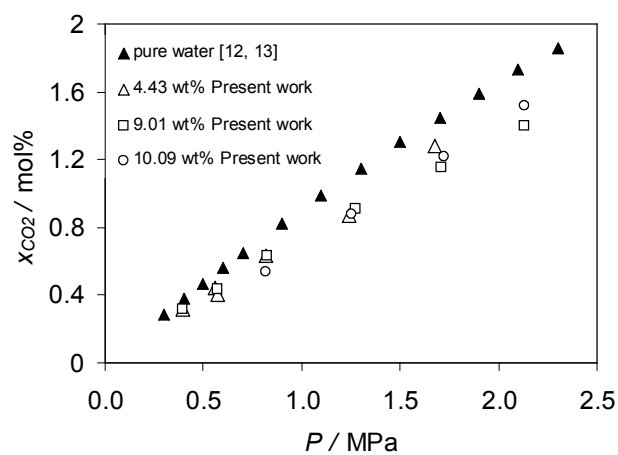


Fig. 3

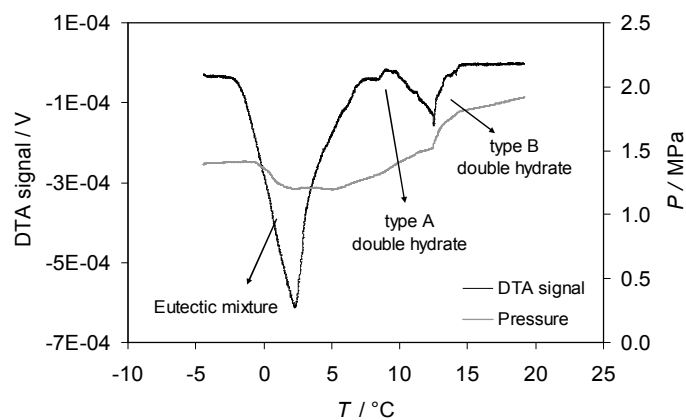


Fig. 4

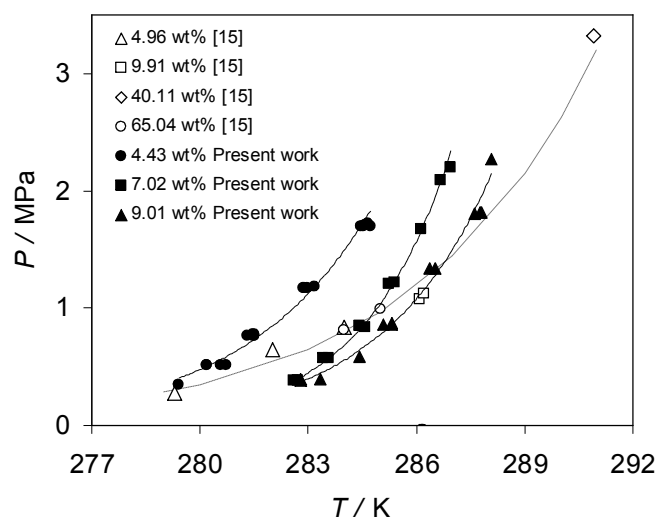


Fig. 5

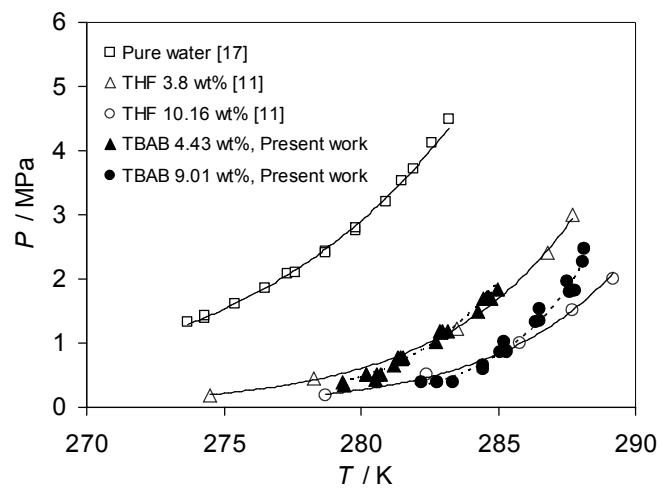


Fig. 6