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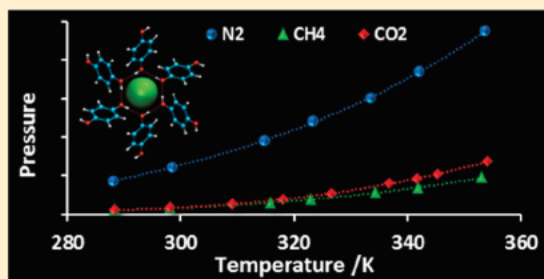
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# Experimental Determination of Phase Equilibria and Occupancies for CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> Hydroquinone Clathrates

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**ABSTRACT:** Hydroquinone (HQ) forms organic clathrates in the presence of various gas molecules in specific thermodynamic conditions. For some systems, clathrate phase equilibrium and occupancy data are very scarce or inexistent in literature to date. This work presents experimental results obtained for the CO<sub>2</sub>–HQ, CH<sub>4</sub>–HQ, and N<sub>2</sub>–HQ clathrates, in an extended range of temperature from about 288 to 354 K. Formation/dissociation pressures, and occupancies at the equilibrium clathrate forming conditions, were determined for these systems. Experiments showing the influence of the crystallization solvent, and the effect of the gas pressure on HQ solubility, were also presented and discussed. A good agreement is obtained between our experimental results and the already published experimental and modeling data. Our results show a clear dependency of the clathrate occupancy with temperature. The equilibrium curves obtained for CO<sub>2</sub>–HQ and CH<sub>4</sub>–HQ clathrates were found to be very close to each other. The results presented in this study, obtained in a relatively large temperature range, are new and important to the field of organic clathrates with potential impact on gas separation, energy storage, and transport.



## 1. INTRODUCTION

Clathrates are solid state host–guest compounds consisting of a network of self associating molecules forming cavities or channels in which guest species can reside.<sup>1</sup> Numerous compounds, including light hydrocarbons, acid gases, organic compounds, inert and rare gases, can be trapped as guest molecules.<sup>2</sup> The most studied clathrates are gas hydrates, where host molecules are water molecules associating by hydrogen bonds and forming cages. When clathrates are formed by organic compounds as host molecules, they are called organic clathrates. Hydroxyaromatic compounds (such as phenol, *para* cresol, and hydroquinone) are well known to form organic clathrates comprising a hydrogen bonded organic framework,<sup>3</sup> and some of them are recognized as an alternative way for gas storage or transportation.<sup>4,5</sup> Recently, some researchers have shown that clathrates could be good media for gas separation thanks to the formation of selective gas clathrates.<sup>6–10</sup> In this way, hydroquinone (HQ) is shown as a good representative of hydroxyaromatic family and a promising candidate for highly selective gas capture and storage.

HQ exists in three different forms:  $\alpha$ ,  $\beta$ , and  $\gamma$  form.  $\alpha$  Hydroquinone ( $\alpha$  HQ) is the stable form at atmospheric temperature and pressure,  $\beta$  hydroquinone ( $\beta$  HQ) is the clathrate formed in well specified conditions of temperature and pressure, and  $\gamma$  hydroquinone ( $\gamma$  HQ) is a metastable form of HQ prepared by sublimation or rapid evaporation of an HQ solution in ether.<sup>3</sup> The monoclinic lattice parameters of  $\gamma$  HQ form, belonging to space group  $P2_1/c$ , are  $a = 8.07$  Å,  $b = 5.20$  Å,  $c = 13.20$  Å, and  $\beta = 107^\circ$ , and this form is not able to

encapsulate guest molecules.<sup>11</sup> The  $\alpha$  HQ form belongs to space group  $R\bar{3}$  with rhombohedral lattices of  $a = 38.5361$  Å and  $c = 5.6641$  Å.<sup>12</sup> According to Powell and co workers' crystallographic studies,<sup>13–15</sup> three crystallographic distinguishable types of  $\beta$  HQ clathrates—designated as types I, II, and III—were established.<sup>16</sup> These types of HQ clathrate are dependent on the nature, the size, and the shape of the encaged guest species.<sup>2,14–16</sup> Small and spherical guest molecules such as xenon and hydrogen sulfide form type I clathrates. Type II clathrates are formed by nonspherical guests slightly larger than those of type I such as hydrogen chloride, methanol, and isocyanomethane. Large molecules such as acetonitrile form type III clathrates. The types I, II, and III  $\beta$  HQ forms belong to space group  $R\bar{3}$ ,  $R3$ , and  $P3$ , respectively.<sup>17</sup> The rhombohedral lattices parameters for all type I  $\beta$  HQ are close to constant value of  $a = 16.60$  Å and  $c = 5.52$  Å.<sup>2,3,7,14</sup> For types II and III  $\beta$  HQ, lattice parameters are affected by cage distortions.<sup>2,3,15,16</sup>

The ideal formula for HQ clathrates is  $3C_6H_4(OH)_2 \cdot xG$  where G is the guest molecule enclosed in the clathrate structure and  $x$  the occupancy of this guest.<sup>1–3,18</sup> Occupancy is the proportion of cavities filled by the gas, ranging from 0 to 1 when the clathrate is guest free or when every cages are occupied, respectively.<sup>1</sup> For HQ clathrate, the ideal stoichiometry

etry corresponds to the ratio 1:3 (one guest molecule per three HQ molecules).

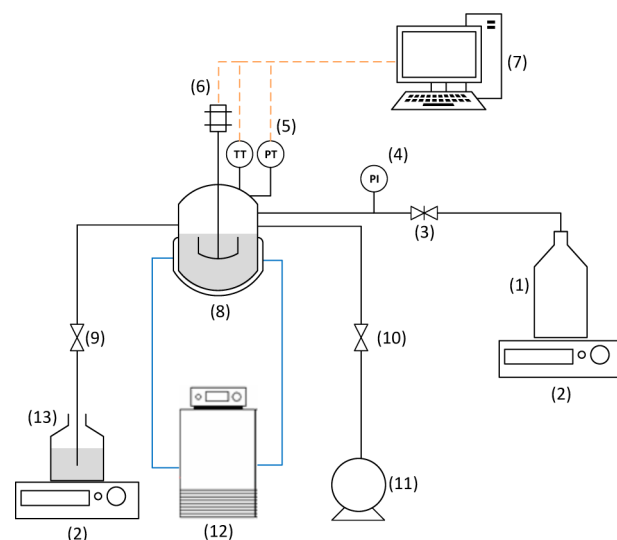
The conditions of transition from  $\alpha$  HQ to  $\beta$  HQ define the triphasic equilibrium curve where the three phases ( $\alpha$  HQ,  $\beta$  HQ, gas) coexist: this line is denoted HQ $_{\alpha}$ –HQ $_{\beta}$ –G in the following. Equilibrium curve is specific to the guest enclosed. For xenon and krypton HQ $_{\alpha}$ –HQ $_{\beta}$ –G equilibrium data are available in literature in the range of temperature from ambient to the HQ fusion point (i.e., 446 K).<sup>19–21</sup> For other gases such as argon (Ar), methane (CH<sub>4</sub>), or nitrogen (N<sub>2</sub>), only a few equilibrium points are available and only for some very limited ranges of temperature.<sup>21–24</sup> Very surprisingly, no data exist or have been published to date for carbon dioxide (CO<sub>2</sub>).

Clathrate equilibrium data and occupancies are information on paramount importance, both for fundamental purposes and in clathrate based practical applications. Therefore, the aim of the present work is to obtain new data of equilibrium and occupancy for CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> HQ clathrates. These data are provided in the range of temperature of interest (from about 288 to 354 K) for potential storage, transportation, or separation applications that could be developed with these compounds. In order to observe the triphasic equilibrium between  $\alpha$  HQ,  $\beta$  HQ, and the gas in a reasonable time, a saturated solution of HQ in a chosen solvent was used as a fourth phase.<sup>22,24</sup>

## 2. EXPERIMENTAL SECTION

**Materials.** Hydroquinone (purity of 99 mol %) was obtained from Acros Organics. The solvents used in the experiments (*n* propanol, isopropanol, butyl acetate) are of analytical reagent grade and were also obtained from Acros Organics. Their mole fraction purities were more than 99%. Argon, methane, nitrogen, and carbon dioxide gases (minimum mole fraction purity of 99.995%) were purchased from Linde Gas SA.

**Apparatus.** The experimental apparatus used for determining equilibrium conditions of clathrates are detailed in Figure 1. The internal capacity of the assembly—connection piping and the reactor volume—is  $384.3 \pm 3.2$  cm<sup>3</sup>, and the whole system is able to run experiments at pressure and temperature up to 20 MPa and 363 K, respectively. The stirred tank reactor was purchased from Parr Company. It is a jacketed high pressure crystallizer, made of 316 stainless steel, which contains a glass cylindrical vessel on the inner reactor shell. The inner surface of this glass vessel has been hydrophobized by using 1H,1H,2H,2H perfluorodecyltrichlorosilane to limit solid adhesion on its surface during the crystallization. The reactor is equipped with a homemade four blade flat turbine as agitator, driven by a motor that is able to maintain a constant rotation speed during the experiment. Two PT100 probes (precision of  $\pm 0.2$  K) were used for measurements of the temperature in the liquid phase and gas phase, respectively. The pressure during the experiment is measured by means of two sensors: a numerical manometer (model LeoII from Keller with an uncertainty of  $\pm 0.01$  MPa) located on the gas flow inlet line, and a 0–10 MPa Keller Model PA33X pressure sensor transducer (uncertainty of  $\pm 0.01$  MPa) located directly on the reactor dome. The temperature in the reactor was maintained at the desired value with a stability of  $\pm 0.02$  K by continuous forced circulation in the reactor jacket of an aqueous solution of propylene glycol using a thermostatic bath (Polystat 37, Fischer Scientific). The reactor was connected to a gas storage tank, a solvent container, and a vacuum pump that



**Figure 1.** Schematic diagram of the experimental apparatus: 1, gas tank; 2, precision balance; 3, fine adjustment valve; 4, numerical manometer; 5, pressure and temperature transmitters; 6, stirring system; 7, data acquisition system; 8, high pressure stirred tank reactor; 9, plug valve of the solvent container; 10, plug valve of the vacuum pump; 11, vacuum pump; 12, thermostatic bath; 13, solvent container.

enables to reach a primary vacuum of 0.0001 MPa in the reactor. The masses of HQ, solvent, and gas introduced into the reactor during the experiment were measured with a Mettler Toledo analytical precision balance (model XP5003S DeltaRange) with an uncertainty of  $\pm 0.0001$  g. Reactor pressure and temperature were recorded for each experiment with an acquisition frequency of 1 Hz using an Agilent station acquisition interface connected to a standard PC.

In order to determine clathrate occupancy in given equilibrium conditions of pressure and temperature, it is first necessary to estimate HQ solubility in the chosen solvent at the same conditions. The experimental apparatus used for this determination was initially developed and used by Torr  et al.<sup>25</sup> to follow up gas hydrate formation. This apparatus consists of a titanium cylindrical vessel as reactor, equipped with two see through sapphire windows of 20 mm diameter each that allow lighting inside the reactor and making visual observations thanks to a CCD camera (OptiaII model from Creative Laboratories). The reactor has a volume of 149 cm<sup>3</sup> and resists pressure up to 20 MPa and temperature up to 363 K. The reactor is placed on a magnetic stirrer (Hei Mix D model from Heidolph), and a magnetic agitator of 20 mm diameter can rotate inside it. The temperature of the reactor is measured with a PT100 probe (precision of  $\pm 0.3$  K) immersed in the liquid phase. The reactor pressure is measured by a 0–20 MPa Keller PA23S pressure sensor transducer (uncertainty of  $\pm 0.01$  MPa). The reactor is linked to the gas storage vessel with an expander valve from Dr ger Tescom, allowing maintaining a constant pressure with a precision of  $\pm 0.01$  MPa. The same vacuum pump, analytical balance, and thermostatic bath described previously were used as experimental apparatus. The whole instrumentation is monitored via a standard PC and a LabView interface, where the temperature and pressure information were sampled every second.

**Procedures.** *Estimation of HQ Solubility under Gas Pressure.* Li and co workers<sup>26</sup> have provided a collection of

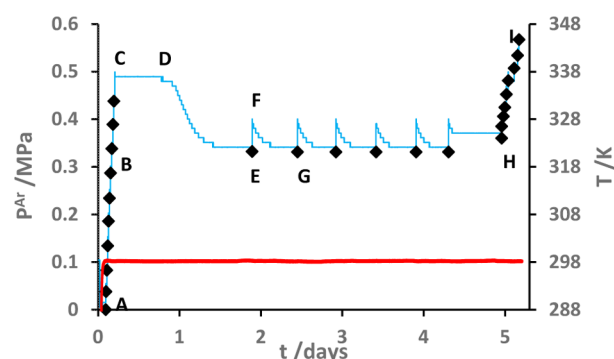


experimental data of solubility of HQ in various solvents (such as water, methanol, ethanol, isopropanol, ethyl acetate, and butyl acetate), and correlated their data set on an extended range of temperature (called Li's correlation in the following). However, their data have been determined at ambient pressure conditions. This parameter being of great importance in the calculation of the clathrate occupancy, one can wonder if the Li's correlation is still valid when the system is pressurized with the gas forming the clathrate. Therefore, to check this point, we have estimated the HQ solubility under pressure with a visual method, for the different gases used in this work. Note that the pressures investigated here were close to the clathrate forming conditions determined in the phase equilibrium experiments, but always inferior to the induction pressure (an overpressure relative to equilibrium) necessary to form the clathrate.

For each experiment, we first fix a target temperature for an expected solubility point (e.g., 298 K). Then, about 20 cm<sup>3</sup> of a solution is prepared with the quantities of HQ and solvent calculated at the target temperature with Li's correlation.<sup>26</sup> The solution is loaded in the reactor, and the temperature is fixed ten degrees below the target temperature (e.g., 288 K if the solubilization temperature expected is 298 K). When the reactor temperature is stable, the agitation is started and the system is put under vacuum to remove the air initially present. Then, the reactor is pressurized with the gas at a value close to the clathrate equilibrium pressure (e.g., 0.604 MPa for N<sub>2</sub> if the solubilization temperature expected from Li's data is 298 K). From this point, the reactor pressure is maintained constant to this value until the end of the experiment. The HQ solvent suspension is then agitated for 2 h to ensure that equilibrium conditions (solubilization of HQ and gas in the solvent) are reached. The temperature is then increased by steps of 0.2 K, and a period of 20 min is let after each temperature increment to ensure that the system has reached the equilibrium. The visual aspect of the suspension inside the reactor is carefully monitored through the reactor window with the camera. We postulated the HQ solubilization temperature to be reached when no more HQ crystallite is visible in the solvent at the naked eye. The temperature is then increased at the same rate up to several degrees from this point to check that no HQ is present (i.e., the solvent must remain perfectly transparent after the solubilization temperature). We are aware that our method cannot provide HQ solubility data with the analytical precision of Li's method. Nevertheless, we believe that this preliminary study is necessary to verify how the gas pressure impacts the HQ solubility, and if Li's correlation can be used or not in our calculations.

**Isothermal Titration Method.** The experimental procedure was inspired by the protocol used by van der Waals and Platteeuw (denoted vdW P in the following) in 1956.<sup>22</sup> This protocol, qualified of an isothermal titration as the formation of the clathrate is made at constant temperature, was used to determine both the triphasic HQ<sub>α</sub>–HQ<sub>β</sub>–G equilibrium curve and the clathrate occupancy. At the beginning of the experiment, about 70 g of solid HQ is loaded into the reactor, and the thermostatic bath temperature is fixed at the desired equilibrium temperature (denoted T<sup>eq</sup>). When the temperature is stable, the reactor is put under vacuum to remove the air initially present: the valves (3) and (9) of Figure 1 are then closed, the valve (10) is opened, and the vacuum pump is turned on. The reactor being under vacuum, the valve (10) is closed and the vacuum pump turned off. The solvent/gas can then be injected due to the pressure difference between the

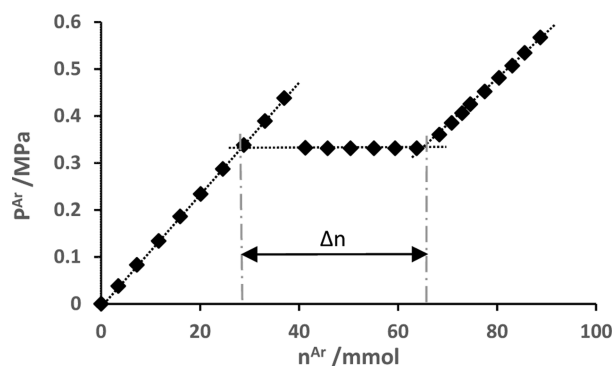
reactor and the solvent container/gas tank. Thus, approximately 110g of solvent is loaded into the reactor by suction under high stirring by opening the valve (9) of Figure 1. At this point, the reactor is filled with an oversaturated solution of HQ—a saturated solution of HQ with a certain amount of solid HQ remaining in suspension—allowing the solvent to be always saturated with HQ even when the clathrate is formed. Accordingly, it is supposed that there is no clathrate formation by dissolved HQ and gas molecules leading to an under saturated HQ solution. This excess amount of HQ, which is directly linked to the quantity of clathrate that will form in the reactor, is dependent on temperature, and more specifically on the solubility of HQ in the solvent. At the temperature of the experiment (T<sup>eq</sup>), the initial vapor pressure of the solution (P<sup>o</sup>) is measured. The equilibrium pressure is then obtained by deducing P<sup>o</sup> from the total pressure measured in the reactor. Then, by successively opening and closing the fine adjustment valve (3) of Figure 1, stepwise additions of gas are done with sufficient time between each to allow the pressure reaching a stabilized value as shown in Figure 2.



**Figure 2.** Example for isothermal titration: blue line, vapor pressure of argon; ◆, equilibrium vapor pressure of argon; red line, temperature as a function of time.

Each mass of gas injected in the reactor is obtained directly by the mass difference noted on the balance after injection. The first part of the experiment (Figure 2 from point A to point B) shows a linear pressure increase with additions of gas. This step corresponds to the solubilization of the gas in the solvent: the only solid phase in the reactional media is  $\alpha$  HQ. After a certain pressure increment, the pressure in the reactor is higher than the equilibrium pressure of the clathrate at T<sup>eq</sup> (point B to point C). The system is, therefore, in a metastable state. When the induction pressure is sufficiently high and after a certain time qualified usually of “induction time” (point C to point D), the reactor pressure begins to decrease as the HQ clathrate of gas is forming (point D to point E), and as no more gas is provided because the reactor is closed. The pressure decreases until the triphasic HQ<sub>α</sub>–HQ<sub>β</sub>–G equilibrium is reached, and stabilizes to this value providing the first value of the equilibrium point of the system (point E). Then, some amount of gas is added to obtain another value of the same equilibrium point: the reactor pressure increases again above the equilibrium (point E to point F) and then decreases (point F to point G) before stabilizing at the same equilibrium pressure. The same process is repeated several times until all the  $\alpha$  HQ is converted to  $\beta$  HQ. At this time, the reactor pressure stabilizes above the plateau (point H), and increases with further gas injections (point H to point I). In order to properly estimate

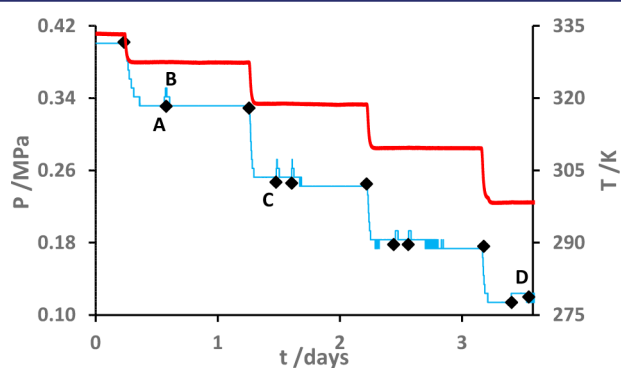
the equilibrium pressure and calculate the clathrate occupancy in these conditions, it is necessary to plot the data in the form of pressure versus quantity of gas added, as shown in Figure 3:



**Figure 3.** Example for isothermal titration: Vapor pressure of argon against quantity of argon added in the reactor loaded by HQ and *n* propanol.

(i) the final equilibrium pressure of the HQ clathrate corresponds to the value of the isobar obtained (horizontal line shown in the Figure 3); and (ii) the molar quantity of gas trapped in the clathrate corresponds to the quantity ( $\Delta n$ ) necessary to convert the excess of  $\alpha$  HQ into  $\beta$  HQ. With this quantity of gas  $\Delta n$ , the clathrate occupancy ( $x$ ) was calculated on the basis of the general HQ clathrate formula  $3C_6H_4(OH)_2 \cdot xG$  (with  $x$  molecule of gas for three molecules of HQ), following the same method as used by vdW P.<sup>22</sup> Excess HQ is obtained by mass balance on HQ in respect to the solubility of HQ in the chosen solvent.

**Temperature-Step Method.** In order to obtain several equilibrium points in the same experiment, we have developed another approach complementary to the isothermal titration method, called the “temperature step method”. This method consists in decreasing step by step the reactor temperature, to reach successive equilibrium points. Prior to such an experiment, it is necessary to measure the initial vapor pressure ( $P^0$ ) of the HQ solution within the temperature range, in order to calculate the gas vapor pressure from the total reactor pressure. The experiment is started with the same protocol as described above for the isothermal titration method. As shown in Figure 4, when the system has reached the first equilibrium point (point A), a small amount of gas is injected (point B) to verify whether the pressure reached is effectively an equilibrium point



**Figure 4.** Example for the temperature step method: blue line, total reactor pressure; ◆, equilibrium pressure; red line, temperature as a function of time.

(namely, the same value of the pressure must be obtained after this gas injection). Then, once the equilibrium point is validated, the reactor temperature is set to a lower value, and this change in temperature forces the system to reach another equilibrium point (point C). By continuing in this way, it is possible to determine several successive equilibrium points, describing a part of the three phase equilibrium curve. This method can be used until the amount of excess HQ in the solution is totally converted to clathrate (e.g., at the point D, the reactor pressure increases with gas injections).

It is worth noting that as all the  $\alpha$  HQ in excess is not converted to clathrate in isothermal conditions, the occupancy (which is a variable depending on temperature) cannot be determined with this method.

### 3. RESULTS AND DISCUSSION

**Selection of the Solvent.** The choice of the solvent is of importance in the experimental methods used in this paper. HQ is soluble in different proportions in various solvents such as alcohols (e.g., ethanol, isopropanol) or esters (e.g., ethyl acetate, butyl acetate). The variation of the HQ solubility with temperature and pressure in function of the chosen solvent must be known to calculate the clathrate occupancy, as discussed in the previous section. By using *n* propanol for their experiments carried out with HQ and argon, vdW P proposed the first values of Ar–HQ clathrate equilibrium pressure and occupancy at 298 K ( $P^{Ar} = 0.344$  MPa and  $x^{Ar} = 34\%$ , respectively).<sup>22</sup> Nevertheless, they gave only one value of solubility of HQ in this solvent at 298 K and atmospheric pressure.<sup>27</sup> In contrary, Li et al.<sup>26</sup> have performed solubility measurements and built correlations to predict the HQ solubility in different solvents at atmospheric pressure in a large range of temperature from 276.65 to 345.10 K. Unfortunately, Li et al. did not provide solubility data for the *n* propanol. Among the solvents studied by Li et al., the ones with relatively low boiling point, such as ethanol or ethyl acetate, which boil at  $351.5 \pm 0.2$  K and  $350.2 \pm 0.2$  K, respectively (calculated average values from NIST), were not considered here. Similarly, isopropanol was not chosen because this solvent may cause complex solute–solvent interactions with HQ.<sup>26</sup> The chosen solvent was finally the butyl acetate for two reasons: (i) a relatively low solubility of HQ (e.g., 11.79 mol % at 298 K)<sup>26</sup> to optimize excess HQ in the reactional medium and (ii) a relatively high boiling temperature at  $399.0 \pm 1.0$  K (calculated average values from NIST).

We verified that the “temperature step method” gives the same results in terms of equilibrium pressure that the “isothermal titration method”. Therefore, we decided to validate the experimental protocol with the “isothermal titration method”, as this method allows providing data both on equilibrium pressures and clathrate occupancies. We have preliminarily tested at 298 K the butyl acetate in replacement to the *n* propanol for the Ar–HQ clathrate system, in respect to the first studies performed by vdW P.<sup>22</sup> We have also tested the robustness and the reproducibility of this method with the two solvents considered on the  $CO_2$ –HQ clathrate system at 298 K. For both solvents, the occupancy has been calculated using the HQ solubility in *n* propanol,<sup>27</sup> and using the Li’s correlation.<sup>26</sup> For this calculation, as vdW P using a solubility determined at atmospheric pressure, we have considered there is no effect of pressure on HQ solubility under 1 atm. The results obtained are presented and compared to literature data in Table 1. Note that the uncertainties of our method have

been estimated including both the precision of all the parameters involved in the calculations and the reproducibility error.

**Table 1. Data of Equilibrium Points and Occupancies of Ar–HQ and CO<sub>2</sub>–HQ Clathrates Obtained at 298 K, Using *n* Propanol and Butyl Acetate as Solvent**

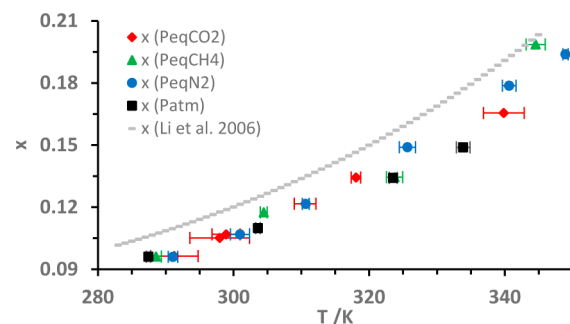
	<i>T</i> /K	<i>P</i> /MPa	<i>θ</i> /%
Ar HQ			
our data with <i>n</i> -propanol	298.0 ± 0.3	0.331 ± 0.012	41.4 ± 1.7
	298.1 ± 0.5	0.321 ± 0.013	39.3 ± 2.3
our data with butyl acetate	297.9 ± 0.5	0.329 ± 0.015	41.0 ± 1.9
experiment from vdW-P (1956) <sup>22</sup>	298.1	0.344	34.0
modeling from Belosludov et al. (1984) <sup>21</sup>	298.0	0.463	39.8
modeling from Conde et al. (2016) <sup>28</sup>	298.0	0.340	36.0
CO <sub>2</sub> HQ			
our data with <i>n</i> -propanol	298.0 ± 0.3	0.083 ± 0.014	54.1 ± 3.4
our data with butyl acetate	298.1 ± 0.3	0.085 ± 0.013	53.6 ± 1.7

First of all, our results for Ar–HQ system with *n* propanol demonstrates that the method used in this work gives fairly reproducible results both for equilibrium pressure (relative dispersion of 1.5%) and clathrate occupancy (relative dispersion of 2.5%). For Ar–HQ clathrates the equilibrium pressures obtained using *n* propanol are in very good agreement with those of vdW P.<sup>22</sup> However, the averaged value of the clathrate occupancy, which is of 40.6 ± 3.2%, was found higher than the only experimental available data in literature for the same system (34% according to vdW P).<sup>22</sup> Note that no uncertainty was given by vdW P for their value. Our experimental value of the occupancy for the Ar–HQ clathrate is consistent with that found (by modeling) by Belosludov et al.<sup>21</sup> at the same temperature.

Regarding now, the equilibrium pressures and occupancies obtained for Ar–HQ or CO<sub>2</sub>–HQ clathrates with *n* propanol and butyl acetate, we can confirm the good reproducibility of these experiments, and particularly that there is no visible influence of the used solvent. The relative dispersion of our results obtained is lower than 1.2% when switching from one solvent to the other. Therefore, the butyl acetate was used in replacement of the *n* propanol in all isothermal titration experiments presented in the following of this paper.

**Influence of the Gas Pressure on the HQ Solubility in Butyl Acetate.** To check the reliability of the Li’s correlation<sup>26</sup> for predicting the HQ solubility in conditions where the system is under pressure, experiments were performed with the three gases (CO<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub>) and butyl acetate as the solvent. The solubility results obtained with the three guests are plotted in Figure 5.

Regarding our solubility data obtained at atmospheric pressure, compared to the predictions of Li’s correlation,<sup>26</sup> it is clear that our visual observation method underestimates HQ solubility of about 10%. Nevertheless, our experimental data well reproduce the temperature dependence described by Li’s correlation. Concerning HQ solubility determined under gas pressure, it is worth noting that there is no (or slightly) effect of the gas pressure on the HQ solubility in the range of temperature and pressure used in this work. Accordingly, we have concluded that the Li’s correlation<sup>26</sup> can be used in this



**Figure 5.** HQ mole fraction solubility in butyl acetate function of temperature. Solubility values at atmospheric pressure: ■, our data; —, Li’s correlation.<sup>26</sup> Solubility values under gas pressure of: ♦, CO<sub>2</sub>; ▲, CH<sub>4</sub>; ●, N<sub>2</sub>.

work to determine the HQ solubility in butyl acetate, in clathrate forming conditions.

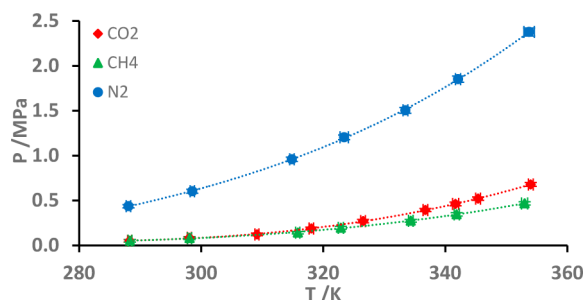
**Equilibrium Points and Occupancies.** The experimental equilibrium data and clathrate occupancies for the CO<sub>2</sub>–HQ, CH<sub>4</sub>–HQ, and N<sub>2</sub>–HQ systems obtained in this work are presented in Table 2. The corresponding equilibrium curves (i.e., the equilibrium pressure versus temperature), and the variation of the clathrate occupancy with temperature are shown in Figures 6 and 7, respectively.

Interestingly, although CH<sub>4</sub> and CO<sub>2</sub> are guests of different chemical nature, shape and size—the spherical CH<sub>4</sub> molecule

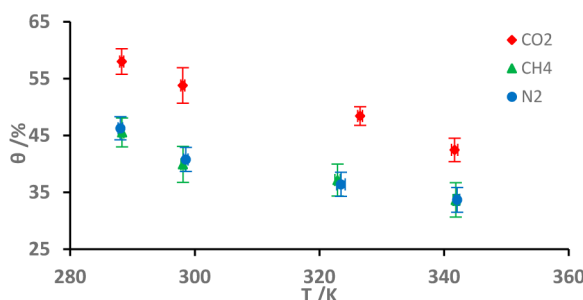
**Table 2. Equilibrium Points and Occupancies of Ar–HQ, CO<sub>2</sub>–HQ, CH<sub>4</sub>–HQ, and N<sub>2</sub>–HQ Clathrates Obtained by Isothermal Titration and “Temperature Step” Method<sup>a</sup>**

method	<i>T</i> /K	<i>P</i> /MPa	<i>θ</i> /%
Ar HQ			
IT	298.0 ± 0.5	0.327 ± 0.019	40.6 ± 3.2
CO <sub>2</sub> HQ			
IT	288.3 ± 0.3	0.052 ± 0.015	58.0 ± 2.2
IT	298.1 ± 0.3	0.084 ± 0.015	53.8 ± 3.1
TS	309.1 ± 0.3	0.123 ± 0.014	
TS	318.1 ± 0.4	0.188 ± 0.015	
IT	326.5 ± 0.4	0.271 ± 0.019	48.4 ± 1.6
TS	336.7 ± 0.4	0.394 ± 0.018	
IT	341.7 ± 0.5	0.462 ± 0.020	42.5 ± 2.1
TS	345.4 ± 0.4	0.522 ± 0.019	
TS	354.0 ± 0.4	0.679 ± 0.021	
CH <sub>4</sub> HQ			
IT	288.3 ± 0.3	0.052 ± 0.015	45.5 ± 2.5
IT	298.1 ± 0.3	0.082 ± 0.015	39.9 ± 3.2
TS	315.8 ± 0.3	0.142 ± 0.014	
IT	322.9 ± 0.4	0.196 ± 0.015	37.2 ± 2.8
TS	334.3 ± 0.4	0.275 ± 0.015	
IT	341.9 ± 0.4	0.346 ± 0.018	33.7 ± 3.0
TS	353.0 ± 0.5	0.468 ± 0.018	
N <sub>2</sub> HQ			
IT	288.1 ± 0.4	0.437 ± 0.018	46.3 ± 2.0
IT	298.5 ± 0.4	0.604 ± 0.022	40.8 ± 2.1
TS	314.9 ± 0.4	0.959 ± 0.024	
IT	323.4 ± 0.7	1.204 ± 0.026	36.4 ± 2.1
TS	333.5 ± 0.4	1.505 ± 0.032	
IT	342.1 ± 0.4	1.852 ± 0.035	33.7 ± 2.2
IT	353.7 ± 0.8	2.377 ± 0.045	

<sup>a</sup>TS = “temperature step” method; IT = isothermal titration.



**Figure 6.** Clathrate equilibrium pressure function of temperature for the different guests:  $\blacklozenge$ ,  $\text{CO}_2$ -HQ;  $\blacktriangle$ ,  $\text{CH}_4$ -HQ;  $\bullet$ ,  $\text{N}_2$ -HQ clathrates.



**Figure 7.** Clathrate occupancy function of temperature for the different guests:  $\blacklozenge$ ,  $\text{CO}_2$ -HQ;  $\blacktriangle$ ,  $\text{CH}_4$ -HQ;  $\bullet$ ,  $\text{N}_2$ -HQ clathrates.

forms HQ clathrate where the cavity is supposed not to be deformed, whereas the linear  $\text{CO}_2$  molecule forms a HQ clathrate characterized by a distorted cavity<sup>29</sup>—their equilibrium curves are close each other (see Figure 6). Similarly to the Ar-HQ system, HQ clathrates formed with  $\text{N}_2$  are obtained with a higher pressure than for  $\text{CO}_2$  and  $\text{CH}_4$ . This observation could result from the difference in dipole-dipole interactions between the guest and the  $\beta$  HQ lattice.<sup>23,30–32</sup> For Ar-HQ and  $\text{N}_2$ -HQ clathrate, it is worth noting that dipole-dipole forces are absent,<sup>29,33</sup> while these forces are likely to be present for  $\text{CO}_2$  and  $\text{CH}_4$  HQ clathrates coupled to possible guest-guest interactions.<sup>33</sup>

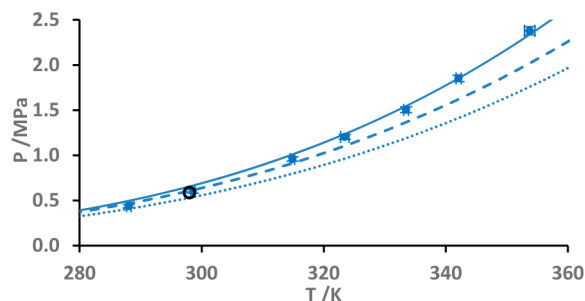
Regarding the values of clathrate occupancy in Table 2 and the plots shown in Figure 7, the occupancy decreases with temperature for the three systems studied, in good agreement with observations and simulations results reported previously in the literature.<sup>19–21,24,28</sup> The occupancies for the  $\text{CH}_4$ -HQ and  $\text{N}_2$ -HQ clathrates are found very close each other in the range of temperature investigated in this work. Our observations agree with the tendencies reported by Conde et al., who have recently studied these systems (except the HQ clathrate formed with the  $\text{CO}_2$ ) by thermodynamic modeling.<sup>28</sup>

Our results seem also to corroborate one of the main assumptions proposed by vdW P<sup>22,23</sup> for their model, which was to consider that the occupancy (at a given temperature) is the same for all HQ clathrates with undistorted lattices. However, we believe that this observation should not be generalized to all the guests forming this clathrate structure, as both experimental and theoretical other studies support the inverse position,<sup>19,20,24,28</sup> that is, that the occupancy is guest dependent.

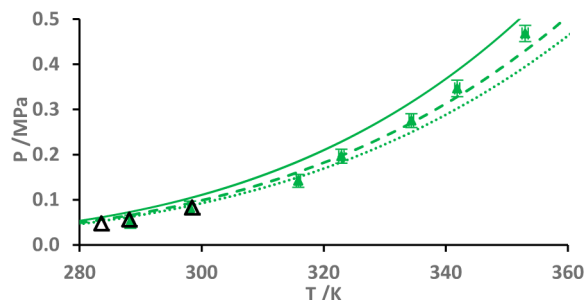
It is very interesting to remark that the occupancies obtained for  $\text{CO}_2$ -HQ clathrate are much higher than those obtained for  $\text{N}_2$ -HQ and  $\text{CH}_4$ -HQ clathrates. For example, at 288 K, the occupancy is  $58.0 \pm 2.2\%$  for  $\text{CO}_2$  against  $45.5 \pm 2.5\%$  for  $\text{CH}_4$ ,

and  $46.3 \pm 2.0\%$  for  $\text{N}_2$  (corresponding to an increase of more than 25% for the  $\text{CO}_2$ -HQ system). Note that  $\text{CO}_2$ -HQ clathrates have distorted cavities. One would notice that a larger value of occupancy was already observed for another HQ clathrate with distorted cavity<sup>23</sup> (e.g., occupancy of 47.4% for methanol-HQ clathrate). Thus, the high occupancies of the  $\text{CO}_2$ -HQ clathrates might be ascribed to the lattice distortion. However, as a very limited information is actually available in the literature concerning the  $\text{CO}_2$  clathrate, further fundamental work is required to better understand this system.

We have compared in Figures 8 and 9 our equilibrium data with modeling predictions obtained for  $\text{N}_2$ -HQ and  $\text{CH}_4$ -HQ



**Figure 8.** Equilibrium data for  $\text{N}_2$ -HQ clathrates:  $\bullet$ , our data;  $\circ$ , experimental data from vdW P;<sup>23</sup> modeling data from Conde et al.<sup>28</sup> using Lennard Jones potential parameters obtained from vdW P<sup>23</sup> (dashed line), Talu and Myers<sup>35</sup> (dotted line), and Cuadros et al.<sup>36</sup> (solid line).



**Figure 9.** Equilibrium data for  $\text{CH}_4$ -HQ clathrates;  $\blacktriangle$ , our data;  $\triangle$ , experimental data from Deming et al.;<sup>24</sup> modeling data from Conde et al.<sup>28</sup> using Lennard Jones potential parameters obtained from vdW P<sup>23</sup> (dashed line), Martin and Siepmann<sup>34</sup> (dotted line), and Cuadros et al.<sup>36</sup> (solid line).

clathrates, respectively. The comparisons were done both to experimental data values found in literature and to predictions of the model developed recently by Conde et al.<sup>28</sup> (which is an extended version of the original vdW P model).

Our experimental equilibrium pressure for the  $\text{CH}_4$ -HQ clathrate of  $0.082 \pm 0.015$  MPa at  $298.1 \pm 0.3$  K is in good agreement with the results of Deming et al.<sup>24</sup> who gave an experimental value of 0.084079 MPa at the same temperature. For the  $\text{N}_2$ -HQ clathrate, our value of  $0.604 \pm 0.022$  MPa at  $298.5 \pm 0.4$  K also agrees with those found experimentally by vdW P (0.58754 MPa at 298 K).<sup>23</sup>

In Figures 8 and 9, the equilibrium pressures and temperatures calculated using the model of Conde et al.<sup>28</sup> are compared to experimental data on a large temperature range for  $\text{CH}_4$ -HQ and  $\text{N}_2$ -HQ clathrates. Indeed, in ref 28 such a comparison could only be made for krypton and xenon HQ clathrates due to the lack of experimental data for the other



guests. In the original model of Conde et al.,<sup>28</sup> the interaction between the guest and HQ and the guest–guest interactions are described with a Lennard Jones (LJ) potential. However, several sets of LJ parameters are available in the literature for CH<sub>4</sub> and N<sub>2</sub>. Hence, three sets have been tested in this work (see Table 3): (i) the one originally proposed by vdW P,<sup>23</sup> (ii)

**Table 3. Lennard Jones Potential Parameters for N<sub>2</sub> and CH<sub>4</sub> Molecules**

	N <sub>2</sub>		CH <sub>4</sub>	
	$\sigma/\text{nm}$	$(\epsilon/k_B)/\text{K}$	$\sigma/\text{nm}$	$(\epsilon/k_B)/\text{K}$
vdW-P <sup>23</sup>	0.3698	95.05	0.3810	142.70
Martin and Siepmann <sup>34</sup>			0.3730	148.00
Talu and Myers <sup>35</sup>	0.3613	100.20		
Cuadros et al. <sup>36</sup>	0.3919	91.85	0.4015	140.42

most recent ones based on fitting on molecular simulation results,<sup>34,35</sup> (iii) the one of Cuadros et al.<sup>36</sup> who have used an alternative fitting procedure based on a real equation of state. One can see that the best agreement between the modeled and experimental dissociation pressures is obtained when the LJ parameters of Cuadros et al. are used, whereas the dissociation pressures computed with the LJ parameters obtained from molecular simulations are systematically underestimated. In this way, our experimental data could be used to discriminate between the different sets of parameters.

If we compare our experimental values of occupancy to literature data, the agreement is also fairly good for CH<sub>4</sub>–HQ clathrates. Accordingly, Deming et al.<sup>24</sup> found an experimental occupancy of 39.1% at 298.1 K and the model of Conde et al.<sup>28</sup> gives a value of 37% (we found  $39.9 \pm 3.2\%$  at  $298.1 \pm 0.3$  K). For N<sub>2</sub>–HQ clathrates, the model of Conde et al.<sup>28</sup> gives slightly lower values of 36% at the same temperature than the experiment (we have obtained  $40.8 \pm 2.1\%$  at  $298.5 \pm 0.4$  K).

Therefore, we can conclude that the comparison of our data with the existing experimental and theoretical information available on these clathrate systems gives a fairly satisfactory agreement, both in terms of clathrate phase equilibria and occupancy.

Finally, as most of the recent studies have been carried out only with HQ and gases (without solvent),<sup>4–10</sup> an additional experiment has been performed in these conditions to check if the thermodynamic equilibrium obtained was the same than the one obtained when HQ is dissolved in butyl acetate. The same quantity of HQ was used for this experiment and CH<sub>4</sub> was the selected gas. We have obtained after 12 days of reaction at  $T = 322.9 \pm 0.4$  K an equilibrium pressure of  $0.202 \pm 0.017$  MPa (value confirmed by a second gas injection). In comparison, the experiment carried out at the same temperature in the presence of butyl acetate (see Table 2) gave an equilibrium pressure of  $0.196 \pm 0.015$  MPa after approximately 4 h of reaction. Therefore, it can be concluded that, on a thermodynamic point of view, the HQ<sub>a</sub>–HQ<sub>b</sub>–G equilibrium is the same with and without solvent. However, on a kinetic point of view, the time to form the clathrate was drastically reduced in the presence of the solvent. This observation on kinetics have been already pointed out in literature for CH<sub>4</sub>–HQ and Ar–HQ clathrates in the presence of *n* propanol as a solvent.<sup>22,24</sup> However, further work with other gases and solvents would be necessary to generalize this conclusion.

## 4. CONCLUSION

In this work, we have studied the equilibrium conditions and occupancies of CO<sub>2</sub>–HQ, CH<sub>4</sub>–HQ, and N<sub>2</sub>–HQ clathrates in a temperature range from about 288 to 354 K.

Experiments performed with different solvents demonstrate that the butyl acetate can be used in replacement to *n* propanol (used initially by vdW P) for easily crystallizing the HQ gas clathrates, as there is no measurable effect of the solvent (between the two tested) on the equilibrium points and occupancies found for the Ar–HQ and the CO<sub>2</sub>–HQ clathrates.

The HQ solubility in butyl acetate was measured under gas pressure close to clathrate forming conditions, showing there is no significant effect of the gas on the HQ solubility in the range of temperature tested in this work. Therefore, Li's correlation can be used for clathrate occupancy calculations.

We have produced in this paper an extended data set of clathrate equilibrium pressures and occupancies for the three following guests CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>. The comparison of our data with the scarce existing experimental and modeling data available in literature, gives fairly good agreement, both in terms of clathrate phase equilibria and occupancy. Our results showed that CO<sub>2</sub>–HQ and CH<sub>4</sub>–HQ clathrates form at milder conditions (lower *P* and *T*) than N<sub>2</sub>–HQ clathrate. This observation would suggest a non negligible influence of dipole–dipole interactions between the enclosed guest molecules and the  $\beta$  HQ lattice, for CH<sub>4</sub> and CO<sub>2</sub> as guests. Moreover, our experimental data have shown to be a useful way of choosing the good LJ set of parameters to be used in the modeling.

In addition, the clathrate occupancy was found temperature dependent, in agreement with previous experimental and modeling tendencies already published in literature. Interestingly, although the occupancies of CH<sub>4</sub>–HQ and N<sub>2</sub>–HQ clathrates were found of the same order of magnitude at the same temperature, the storage capacity of CO<sub>2</sub>–HQ clathrate at equilibrium was found higher. This result may be possibly due to the lattice distortion necessary to accommodate the CO<sub>2</sub> molecules or to specific van der Waals or Coulomb interactions between this guest and HQ.

Finally, the equilibrium curves obtained for CO<sub>2</sub>–HQ and CH<sub>4</sub>–HQ clathrates were found very close to each other. In addition, it was shown for the CH<sub>4</sub>–HQ clathrate that the dissociation pressure (obtained at the same temperature) with (using butyl acetate) and without solvent (direct gas/solid reaction) was identical, demonstrating that the presence of the solvent has no influence on the HQ<sub>a</sub>–HQ<sub>b</sub>–G triphasic equilibrium. This result suggests that a thermodynamic process is likely not to be responsible for the relative high selectivity toward CO<sub>2</sub> that has been recently found for the separation of CO<sub>2</sub>/CH<sub>4</sub> by HQ clathrate formation.<sup>7</sup> Further work is indeed necessary to better understand this point, and complementary experiments and modeling work are currently in progress in this sense in our laboratory.

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## Notes

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## ■ ABBREVIATIONS

HQ, hydroquinone; CO<sub>2</sub>, carbon dioxide; CH<sub>4</sub>, methane; N<sub>2</sub>, nitrogen; Ar, argon

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