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# CO<sub>2</sub> Capture and Storage by Hydroquinone Clathrate Formation: Thermodynamic and Kinetic Studies.

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## Abstract

Hydroquinone (HQ) can form a gas clathrate in specific pressure and temperature conditions in the presence of CO<sub>2</sub> molecules. This study presents experimental data of clathrate phase equilibrium and storage capacity for the CO<sub>2</sub>-HQ system in the range of temperature from about 288 to 354 K. Intercalation enthalpy and entropy are determined using the obtained equilibrium data and the Langmuir adsorption model. On a kinetic point of view, CO<sub>2</sub>-HQ clathrate formation by solid/gas reaction revealed a non-negligible effect of textural parameters on enclathration rate.

## Introduction

Gas clathrates are inclusion compounds formed with host molecules self-associating and forming cages, able to retain low molecular-weight guest molecules of gas, which have recently been highlighted as an alternative way for gas storage, transportation and separation [1-2]. Gas hydrates show high gas storage capacity. However, for potential industrial applications, the hydrate-based processes require a non-negligible energetic cost as gas hydrates are usually formed at low temperature, typically a few degrees above 273 K, and high pressure of several MPa [3]. To overcome this problem, hydroquinone (HQ) has been pointed out because of its capability to form organic clathrates over a wide range of temperature and at moderate pressure (a few MPa) [4-6]. The stable form of HQ at ambient conditions of pressure and temperature is the  $\alpha$ -HQ. Whereas, the clathrate form is the  $\beta$ -HQ. The maximum storage capacity of  $\beta$ -HQ is defined by its ideal stoichiometry of 1 molecule of gas per 3 molecules of HQ, if all the cavities are filled by one guest molecule [7]. Thus, for CO<sub>2</sub>-HQ clathrates the maximum theoretical quantity of gas which can be stored is 67.8 L (STP) / kg<sup>HQ</sup>.

This work presents experimental data on phase equilibria and kinetics of CO<sub>2</sub>-HQ clathrate formation. Such results could be of interest for potential gas storage, transportation, or separation applications that could be developed with this compound. The equilibrium curve, the clathrate occupancy and the intercalation enthalpy and entropy are determined in the range of temperature from about 288 to 354 K. Ways for kinetic improvements are proposed and discussed. Interestingly, the use of HQ-silica composite materials as reactive medium has shown that the kinetic of HQ clathrate formation can be significantly improved.

## Experimental section

### Materials

HQ with purity of 99.5 mol% is provided by Acros Organics. The solvents used for the titration and impregnation experiments are butyl acetate and absolute ethanol (purities higher than 99 mol%). CO<sub>2</sub> gas used for the experiments (mole fraction purity of 99.995%) is purchased from Linde Gas SA. The porous supports are analytical grade spherical silica particles (SiliaSphere®) sizing 200-500  $\mu$ m with pore size of 100 nm provided by SiliCycle.

## Apparatus and Procedures

The experimental apparatus used for determining equilibrium conditions of clathrates is composed by a jacketed and stirred high pressure crystallizer connected to a gas storage tank, a solvent container, and a vacuum pump [8]. This experimental set-up allows achieving isothermal titration [8], which is the method used to determine both the  $HQ_{\beta}$ - $HQ_{\alpha}$ - $CO_2$  equilibrium curve and the clathrate occupancy.

The capture kinetic and the gas storage capacity measurements are performed by a gravimetric method [9] at 3.0 MPa and 323 K, using a Rubotherm magnetic suspension balance. For these measurements, the HQ is conditioned in two ways in an attempt to increase the clathrate formation kinetics. Pure HQ is ground or deposited on porous support.

The HQ deposition on porous silica support is performed in fluidized bed in a dry impregnation process [10]. This method consists in intermittently spraying a warm fluidized bed of porous silica particles with a HQ solution, allowing the coupling of the HQ solution penetration in the particle porosity and the solvent evaporation.

## Results and discussion

### Phase Equilibria and occupancies

The experimental equilibrium data for the  $CO_2$ -HQ systems are obtained in this work from isothermal titration experiments [8]. The equilibrium curve and the clathrate occupancies at these equilibrium conditions are shown in Figure 1. Compared to the  $CO_2$  hydrates equilibrium curve [11-12], it can be noted that the  $CO_2$ -HQ clathrates can be formed over a wide range of temperature and at pressures not exceeding 1 MPa for temperatures close to 360 K. Regarding the obtained clathrate occupancies, it is obvious that these ones are temperature dependent. The  $CO_2$ -HQ clathrate occupancy decreases with temperature, as already pointed out in literature for other HQ clathrates [13].

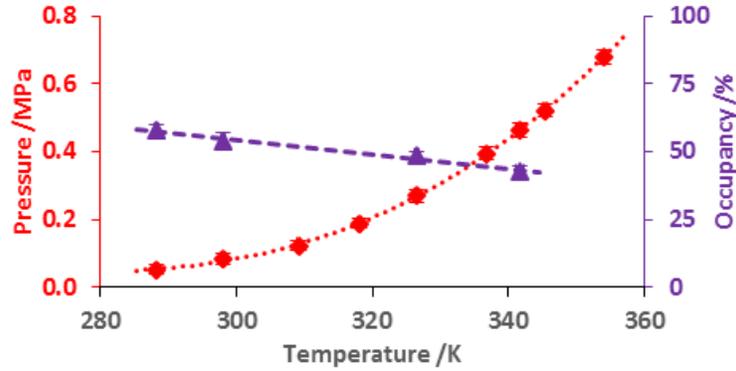
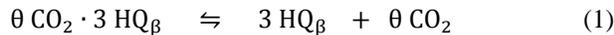


Figure 1: Equilibrium data for  $CO_2$ -HQ system:  $\blacklozenge$ , clathrate equilibrium curve;  $\blacktriangle$ , clathrate occupancies as a function of temperature.

As there is an analogy between enclathration and adsorption, the gas-clathrate equilibrium obey a Langmuir type isotherm [13-15], where the involved reaction, given by Equation 1, corresponds to the liberation of the  $CO_2$  guest molecules from the  $\beta$ -HQ host lattice.



The Langmuir constant  $C_{lang}$  related to this reaction (i.e. the thermodynamic equilibrium constant) depends on clathrate occupancy  $\theta$  and equilibrium pressure  $P_{eq}$ , as described by Equation 2.

$$C_{lang} = P_{eq} \cdot (1 - \theta)/\theta \quad (2)$$

Thus, the intercalation enthalpy and entropy can be determined from the slope and the intercept of the linear fit of the logarithm of the Langmuir constant as a function of the inverse of equilibrium temperature (Figure 2) [13-14]. The

obtained enthalpy is  $42.3 \pm 4.0 \text{ kJ/mol}^{\text{CO}_2}$  ( $14.1 \pm 1.3 \text{ kJ/mol}^{\text{HQ}}$ ) and the associated entropy is  $235 \pm 11 \text{ J/mol}^{\text{CO}_2/\text{K}}$  ( $78 \pm 4 \text{ J/mol}^{\text{HQ}/\text{K}}$ ). To determine the total dissociation enthalpy of the  $\text{CO}_2$ -HQ clathrate, it is necessary to consider the enthalpy of the reversion of the residual  $\beta$ -HQ to the  $\alpha$ -HQ structure of about  $-0.67 \text{ kJ/mol}^{\text{HQ}}$  [16]. As a result, these data indicate that the  $\text{CO}_2$  can be recovered more easily from  $\text{CO}_2$ -HQ clathrates than from  $\text{CO}_2$  hydrates as the dissociation enthalpy is about  $60.6 \pm 1.8 \text{ kJ/mol}^{\text{CO}_2}$  ( $10.0 \pm 0.3 \text{ kJ/mol}^{\text{H}_2\text{O}}$ ) between the quadruples points Q1 and Q2 of this system [17].

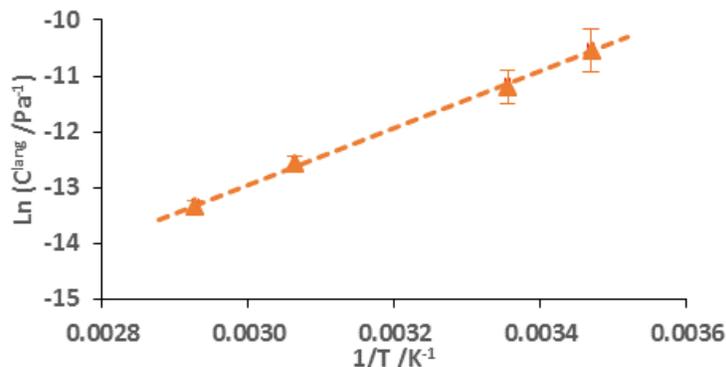


Figure 2: Linear fit of the logarithm of the Langmuir constants of  $\text{CO}_2$ -HQ clathrates as a function of the inverse of temperature.

### Kinetic aspects

When the gas clathrate is formed by direct gas/solid reaction between the  $\text{CO}_2$  and the HQ, the clathrate formation kinetics seems to be enhanced by increasing the gas/solid contact area [4-6]. Thus, working on the HQ conditioning (i.e. the increase of the specific area of the media and the improvement of the contact area between the  $\text{CO}_2$  and the HQ) is very important to achieve rapid enclathration kinetics.

In this work, we have tested and compared the kinetic performances of HQ powder and of a HQ-silica composite material. The grinding of HQ gives a powder with a particle size of about  $100 \mu\text{m}$ . The HQ deposition on porous silica support allows developing a composite material having the HQ content of  $0.44 \text{ g}^{\text{HQ}}/\text{g}^{\text{Silica}}$ .

As shown in Figure 3 by SEM images of the obtained composite, it appears clearly that HQ coats uniformly the external surface of the silica particle. Moreover, HQ crystals could be present in the  $100 \text{ nm}$  pores. Indeed, as suggested by Hemati *et al.* [10] the growth phenomenon does not arise before the full filling of internal porosity.

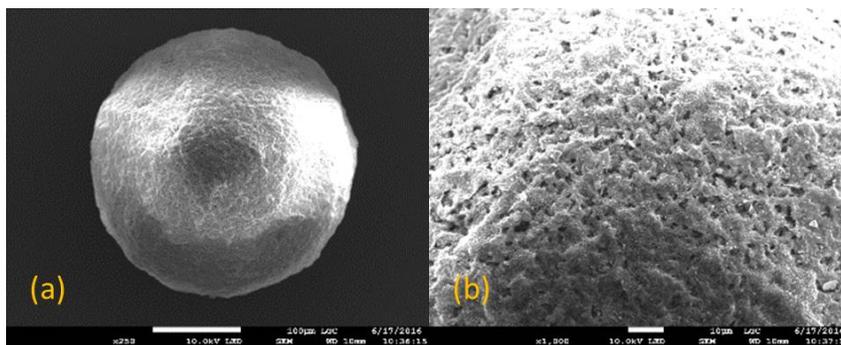


Figure 3: SEM images of HQ-silica composite material: (a) full particle and (b) external surface.

The native, ground, and impregnated HQ are evaluated as media in  $\text{CO}_2$  capture experiments. The amount of  $\text{CO}_2$  captured by enclathration as a function of time is shown in Figure 4. For HQ-silica composite materials, the amount of  $\text{CO}_2$  likely to be adsorbed on native silica (i.e.  $0.34 \text{ mol}^{\text{CO}_2}/\text{kg}^{\text{Silica}}$ ) has been deduced from the total  $\text{CO}_2$  gas

captured. It is worth noting that the two conditionings improve the kinetic of clathrate formation, which highlights the importance of CO<sub>2</sub>/HQ contact area.

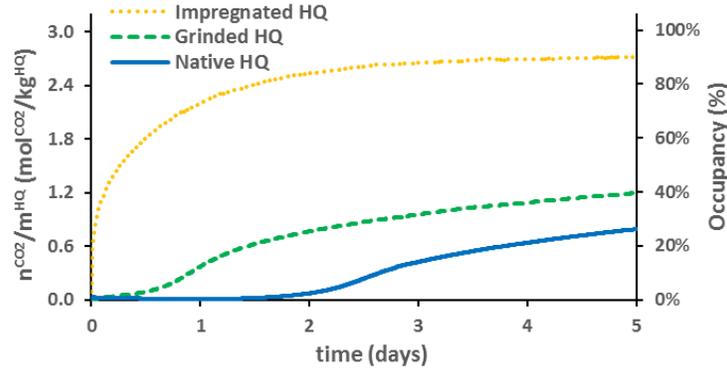


Figure 4: Molar quantity of CO<sub>2</sub> captured by enclathration as a function of time normalized by mass of HQ: (full line) native HQ, (dashed line) ground HQ, and (dotted line) HQ impregnated on silica particles.

Table 1 presents the kinetic criteria deduced from the gas capture measurements: (i) the reaction rate for the CO<sub>2</sub> solubilization in the  $\alpha$ -HQ, (ii) the induction time, (iii) the enclathration reaction rate, and (iv) the characteristic time at which the clathrate occupancy is 50%.

Compared to native HQ, although grinding of HQ seems kinetically interesting, it is obvious that the HQ-silica composite material is the most efficient medium for enclathration. Indeed, for this reactive medium there is no induction period, the enclathration reaction rate is increased by a factor 52, and the time to fill 50% of the clathrate cavities is decreased by a factor 55 compared to native HQ.

Moreover, for HQ-silica composite material, the system reaches an equilibrium value of clathrate occupancy of 0.89 after approximately 3.5 days, whereas the clathrate occupancies are 0.18 and 0.34 for native and ground HQ, respectively at the same time. After about 1 month of reaction, it is found occupancies of 0.63 and 0.71 for native and ground HQ, respectively. These values are in agreement with the ones previously found for CO<sub>2</sub>-HQ clathrates mono-crystals synthesized by crystallization from solvent [18].

Table 1: Kinetic data on the CO<sub>2</sub> capture by HQ clathrate formation.

HQ conditioning	$r_0$ (mmol <sup>CO2</sup> /kg <sup>HQ</sup> /min)	$t^{ind}$ (h)	$r_c$ (mmol <sup>CO2</sup> /kg <sup>HQ</sup> /min)	$t_c^{50}$ (h)
Native	0.02	23.4	0.32	356.5
Grinding	0.16	4.2	0.52	218.9
Impregnation	-	-	16.5	6.5

## Conclusion

This study brings some information on the potentiality of HQ clathrates for CO<sub>2</sub> capture and storage process. The measured equilibrium conditions suggest the possibility to overcome specific process limitation, as CO<sub>2</sub>-HQ clathrates can be formed in a wide range of temperature (reaching at least 354 K) and at moderate pressure (few MPa). Furthermore, on a kinetic point of view, it is shown that the enclathration kinetic can be improved by a specific conditioning of HQ allowing to increase the gas/solid contact area. The induction period can be avoided with a non-negligible increase of enclathration rate using HQ-silica composite materials. Now, some works are necessary to evaluate the viability and feasibility of such reactive media in clathrate-based processes.

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