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Phase equilibrium properties of CO₂/CH₄ mixed gas hydroquinone clathrates: Experimental data and model predictions

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A B S T R A C T

Hydroquinone (HQ) clathrates seem to be promising inclusion compounds for selective CO₂ capture from gas mixtures. However, to date no phase equilibrium data are known in literature for mixed gas HQ clathrates. This study presents experimental equilibrium pressures obtained within a range of 298–343 K for different CO₂/CH₄ gas mixtures. The clathrate composition is given for each equilibrium point. The capture selectivity is calculated from the molar composition of the CO₂/CH₄ gas mixture in the clathrate and in the gas phase. The results obtained reveal that CH₄ molecules in the CO₂/CH₄ mixtures are preferentially captured at equilibrium conditions. Our experimental data are compared against numerical predictions obtained from thermodynamic modeling using the Conde's model. Very good agreement is found between the calculated and experimental data in terms of clathrate phase equilibria.

Keywords:

Clathrate

Equilibrium

Hydroquinone

Carbon dioxide

Methane

Thermodynamic modeling

1. Introduction

Hydroquinone (α HQ) is capable of forming organic clathrates with species such as CO₂, CH₄, and N₂ in well specified thermodynamic conditions of temperature and pressure [1]. Gaseous molecules (called “guests”) are engaged inside a molecular network formed by HQ molecules (called “hosts”). Clathrates containing different types of guest molecules are called mixed gas clathrates. HQ clathrates (β HQ) have recently received considerable attention in the field of gas separation, as the enclathration can be potentially highly selective to one of the gases initially present in the raw gas mixture [2–7]. The separation of CO₂ from a CO₂/CH₄ gas mixture is particularly important in the areas of energy, the environment and Oil & Gas, where active research is being conducted to find more efficient and economic gas separation processes. Although equilibrium curves of co existing α HQ, β HQ and gas (i.e. the three phase equilibrium line) are known for some pure HQ clathrates containing Xe [8], Kr [9], CO₂ [10], CH₄ [10] and N₂ [10], to date no equilibrium data are reported in literature for mixed gas HQ clathrates. These data are of paramount importance for providing both insights at the fundamental level and engineering data for process design. Therefore, this study presents, for the

first time, equilibrium curves of mixed gas HQ clathrates. Equilibrium data are obtained from isothermal titration experiments [10], in the temperature range of 298–343 K for HQ clathrates formed with CO₂/CH₄ gas mixtures.

A comparison between experimental results and modeled data is given. Thermodynamic modeling is achieved using the model from Conde et al. [11], which was recently used to compute phase equilibria, enthalpies and occupancies of various pure HQ clathrates.

2. Experimental section

2.1. Materials

The Hydroquinone (mole fraction purity of 99.5%) was provided by Acros Organics. Butyl acetate of analytical reagent grade (mole fraction purity higher than 99%) was used as a solvent in the experiments. CO₂/CH₄ gas mixtures with CO₂ mole fractions of 0.2, 0.4, 0.6 and 0.8 (minimum mole fraction purity of 99.995%) were purchased from Linde Gas S.A. The gas mixtures compositions were checked and found in agreement with those given by the supplier specified within a relative standard uncertainty of $\pm 2\%$. The specifications of the chemicals used in this study are also given in Table 1.

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Table 1
Materials used in the study.

Material	Supplier	Purity (mol.%)
Hydroquinone	Acros Organics	99.5
Butyl acetate	Acros Organics	>99
Carbon dioxide/Methane	Linde Gas S.A.	99.995

The chemicals were used as received.

2.2. Apparatus and method

The experimental apparatus was the one initially developed and used by Coupán and coworkers [10] in experiments to obtain the phase equilibria and clathrate occupancies of CO₂, CH₄ and N₂ HQ clathrates by isothermal titration. In short, the set up consists of a jacketed, stirred high pressure crystallizer connected to a gas storage tank, a solvent container, a vacuum pump, and a high pressure gas chromatograph (Agilent, model GC6980) equipped with a capillary column (model HP PLOT Q) and a thermal conductivity detector. The precision of the temperature and pressure measurements is ±0.2 K and ±0.01 MPa, respectively. Refer to [10] for technical details on the apparatus. The masses of HQ, butyl acetate and gas introduced into the reactor were measured using a Mettler Toledo analytical precision balance (model XP5003S DeltaRange) with a standard uncertainty of ±0.0001 g.

The typical experimental procedure is as follows: about 70 g of solid HQ and 110 g of butyl acetate are loaded into the reactor at the targeted equilibrium temperature, leading to a typical HQ concentration of $572 \pm 5 \text{ g}^{\text{HQ}}/\text{l}^{\text{Solvent}}$ (averaged value considering 14 experiments). Then, gas is added incrementally with sufficient time in between to allow the pressure to reach a stabilized value, as shown in Fig. 1. During the first part of the experiment (Fig. 1, from point A to point B), the pressure firsts increases due to the pressurization of the reactor and then decreases to point B due to the dissolution of the gas in the solvent. After this step, there is an induction period (plateau after point B) before the start of the enclathration reaction. The pressure thus decreases once the gas clathrate starts forming until the equilibrium point of the system is reached (point C). Further gas additions make it possible to obtain several points (points D and E) of the same equilibrium. As shown in Fig. 2, a plot of the system pressure versus the amount of gas added allows drawing a single curve where its horizontal part (i.e. the isobar) corresponds logically to the average equilibrium pressure. We know that at each additional gas injection and for each equilibrium point obtained, there is a slight modification of

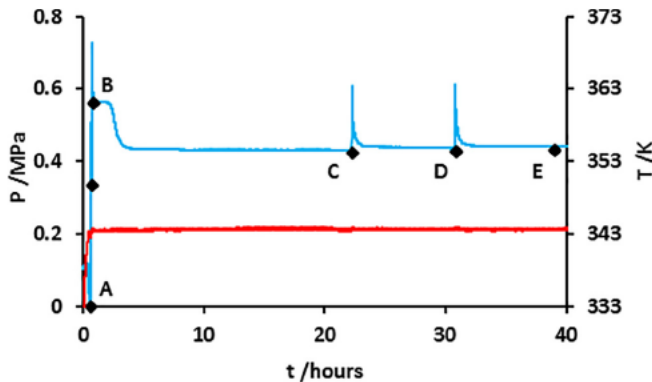


Fig. 1. Example for isothermal titration: (blue line) vapor pressure of the CO₂/CH₄ mixture; ◆, equilibrium vapor pressure of the CO₂/CH₄ mixture; (red line) temperature, as a function of time. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

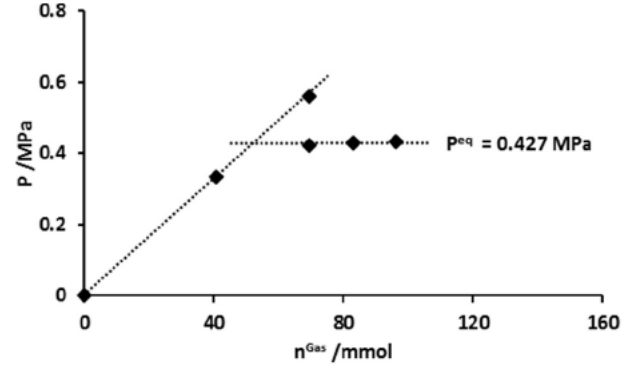


Fig. 2. Example of isothermal titration at 343.7 K: Vapor pressure of CO₂/CH₄ mixture versus the amount of CO₂/CH₄ gas mixture added to the reactor with HQ and butyl acetate load.

the gas composition with a resulting impact on the equilibrium pressure. However, the impact is negligible and falls within the 0.01 MPa standard uncertainty range of the pressure sensor. As the experimental time is quite long, the isobar comprises only three equilibrium points at most (i.e. the reaction is not total), but this is sufficient to determine the corresponding phase equilibrium point. Note that the occupancy cannot be determined here, as not all the α HQ is converted into clathrate.

Additionally, the gas composition has to be measured twice (see Fig. 1): (i) before the start of the enclathration reaction (point B) (i.e. at the induction pressure after the gas dissolution step) and (ii) after thermodynamic equilibrium is reached (points C, D and E). These measurements are used to calculate, by mass balance, the average gas composition in the clathrate and to estimate the capture selectivity. In fact, the decrease of the molar quantity in the gas phase corresponds to the molar quantity of gas enclosed in the clathrate. The amount of gas is given by Eq. (1):

$$n_{\text{clathrate}}^i = n_{\text{gas}}^i \Big|_{t_{\text{ind}}} - n_{\text{gas}}^i \Big|_{t_{\text{eq}}} = \frac{y^i PV}{zRT} \Big|_{t_{\text{ind}}} - \frac{y^i PV}{zRT} \Big|_{t_{\text{eq}}} \quad (1)$$

where the superscript i corresponds to the CO₂ or CH₄ constituent, y^i is the molar composition of the constituent i in the gas mixture, z is the compressibility factor (calculated using the Soave Redlich Kwong equation of state and the van der Waals mixing rules with a binary interaction parameter set to 0.1 [12]), P is the reactor pressure, T is the temperature, V is the volume of the gas phase and t_{ind} and t_{eq} are the times before and after the reaction. Then, the clathrate composition can be obtained by the ratio of the molar quantity of one of the constituents to the total quantity. The CO₂ capture selectivity (also termed the “separation factor” in literature [13]) in the clathrate forming conditions can be obtained from Eq. (2):

$$\text{S.F.}^{\text{CO}_2/\text{CH}_4} = \frac{x^{\text{CO}_2}/(1-x^{\text{CO}_2})}{y^{\text{CO}_2}/(1-y^{\text{CO}_2})} \quad (2)$$

where x^{CO_2} and y^{CO_2} are the CO₂ molar compositions in the CO₂/CH₄ gas mixture in the clathrate and in the gas phase respectively.

3. Thermodynamic modeling

The thermodynamic model is detailed elsewhere [11]. It is a modified version of the traditional van der Waals Platteeuw (vdW P) model which takes into account both the solubility of gases in α HQ and the interactions between the guest molecules. The last difference with the standard version of the vdW P model is that the reference state, initially set to 298 K by van der Waals and Platteeuw, was replaced by the melting point of HQ ($T_0 = 446 \text{ K}$). Thus, the clathrate equilibrium pressures are com

puted by equalizing the two following chemical potential differences between the considered phase and the empty HQ clathrate:

$$\Delta\mu^{\alpha \text{ HQ}}(T, P) = RT \left[\frac{\Delta\mu_0^{\alpha\beta}}{RT_0} - \frac{\Delta H_0^{\alpha\beta}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) + (P - P_0) \frac{\Delta V_0^{\alpha\beta}}{RT} \right] \quad (3)$$

and

$$\Delta\mu^{\beta \text{ HQ}}(T, P) = RT \left[(v^\beta - v^\alpha) \ln(1 - \sum_i \theta_i) - \sum_i \sum_j \frac{\theta_i \theta_j}{2} (v^\beta V_{ij}^\beta - v^\alpha V_{ij}^\alpha) \right] \quad (4)$$

where v is the number of cages per host molecule in the lattices, θ_i is the occupancy factor for each guest i and V_{ij} is the guest-guest contribution to the chemical potential. The occupancies are classically given as a function of the Langmuir constants and the fugacities of the guests as done in the standard version of the vdW P model.

4. Results and discussion

The choice of the solvent and the reliability of the method were previously tested and verified in previous work [10]. The experiments were performed with different CO₂/CH₄ gas mixtures of initial CO₂ mole fractions equal to 0.2, 0.4, 0.6 and 0.8. The obtained clathrate equilibrium points are associated with equilibrium CO₂ mole fractions ranging from 0.15 to 0.75. The experimental equilibrium data and the gas composition before reaction for the different CO₂/CH₄ HQ systems are reported in Table 2. The corresponding equilibrium points (i.e. the equilibrium pressure versus temperature) are shown in Fig. 3, where the data of the pure components [10] CO₂ and CH₄ are superimposed. For the experiments, the errors were estimated taking into account the precision of sensors, the measurement dispersion and the reproducibility error of 1.5%.

As expected, all the obtained equilibrium points are found between the equilibrium curves of the CH₄ HQ and CO₂ HQ systems. We can see that the equilibrium points associated with high CO₂ mole fractions are very close to the CO₂ HQ equilibrium curve and the contrary for equilibrium points associated with high CH₄ mole fractions. It is worth noting that the same observations are made for clathrate hydrates formed from the CO₂/CH₄ gas mixtures [14].

Additionally, our equilibrium data for CO₂/CH₄ mixed HQ clathrates are compared against data obtained using the model in Conde et al. [11] briefly recalled in the previous section. The fugacities of CO₂ and CH₄ are computed with the Soave Redlich Kwong equation of state. The solvent is not considered in the study as it has been previously shown [10] that it has no effect both on the

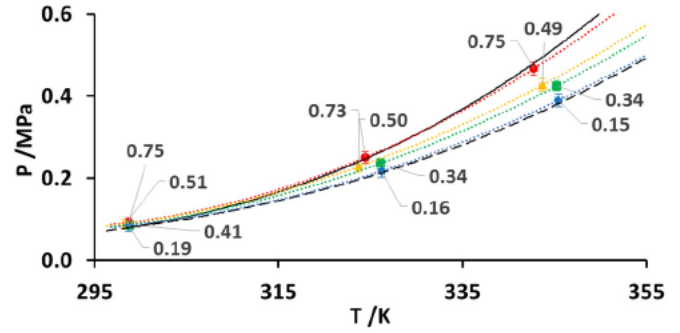


Fig. 3. Clathrate equilibrium pressure as a function of temperature for CO₂/CH₄ mixed-gas HQ clathrates for initial CO₂ mole fractions of 0.2 (blue), 0.4 (green), 0.6 (yellow) and 0.8 (red). Data labels indicate the equilibrium CO₂ mole fraction in the gas phase after the reaction. Equilibrium curve for pure components [10]: CO₂ (full line) and CH₄ (dashed line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

clathrate equilibrium pressures and occupancies. The thermodynamic modeling was performed taking into consideration the same parameters as for the other type I HQ clathrates, such as CH₄ and N₂ (e.g. same 3.95 Å diameter cavity). The Lennard Jones parameter set for CO₂ (i.e. $\sigma = 4.416$ Å and $\varepsilon/k_B = 192.25$ K) is the one given by Tee et al. [15]. A cross interaction parameter of 1.03 was used to consider the deviation from ideality for the CO₂ HQ binary in the Lorentz Berthelot combining rule.

The calculations were performed for 344, 325 and 298 K according to the experimental equilibrium temperatures. The experimental and modeled equilibrium pressures are compared in Fig. 4. Very good agreement is found between experimental and modeled pressures for the CO₂/CH₄ mixed HQ clathrates whereas the model does not consider the atypical behavior of CO₂ cavities (e.g. the CO₂ distorts the HQ clathrate cavities [16]). It is worth noting that the agreement is also fairly good for pure CO₂ (e.g. the experiment at 345.4 K gives an equilibrium pressure of 0.522 ± 0.014 MPa, whereas the modeled pressure at 344 K is 0.514 MPa).

Regarding the clathrate compositions shown in Fig. 5, it appears that the CO₂ mole fraction in the clathrate increases with increasing CO₂ mole fraction in the initial gas mixture. The same trend is observed with the modeling results. Nevertheless, we can see that the thermodynamic model tends to overestimate the quantity of CH₄ in the clathrate. This is not surprising as the Conde et al. model [11] underestimates the occupancy of the pure CO₂ HQ clathrate whereas the occupancy of the pure CH₄ HQ clathrate is perfectly

Table 2
Equilibrium points of CO₂/CH₄-HQ clathrates obtained by isothermal titration: ($y^{\text{CO}_2\text{i}}$) molar composition of the initial gas mixture, (T) temperature; Variables before reaction at the induction time: ($y^{\text{CO}_2\text{ind}}$) molar composition of the gas mixture, and (P_{ind}) induction pressure; Variables after reaction at equilibrium state: ($y^{\text{CO}_2\text{eq}}$) molar composition of the gas mixture in the gas phase, ($x^{\text{CO}_2\text{eq}}$) molar composition of the gas mixture in the clathrate phase, and (P_{eq}) equilibrium pressure.

$y^{\text{CO}_2\text{i}}$	T / K	Before Reaction (at induction time)		After Reaction (at equilibrium)		
		P_{ind} /MPa	$y^{\text{CO}_2\text{ind}}$	P_{eq} /MPa	$y^{\text{CO}_2\text{eq}}$	$x^{\text{CO}_2\text{eq}}$
0.80	298.7 ± 0.3	0.260 ± 0.012	0.610 ± 0.002	0.092 ± 0.013	0.754 ± 0.002	0.51 ± 0.08
0.80	324.4 ± 0.3	0.370 ± 0.012	0.650 ± 0.002	0.250 ± 0.015	0.732 ± 0.002	0.49 ± 0.06
0.80	342.7 ± 0.4	0.737 ± 0.012	0.680 ± 0.002	0.467 ± 0.016	0.748 ± 0.002	0.55 ± 0.04
0.60	298.3 ± 0.3	0.172 ± 0.012	0.380 ± 0.001	0.089 ± 0.013	0.512 ± 0.002	0.22 ± 0.06
0.60	323.7 ± 0.3	0.345 ± 0.012	0.440 ± 0.001	0.229 ± 0.014	0.502 ± 0.002	0.29 ± 0.04
0.60	343.7 ± 0.3	0.569 ± 0.012	0.432 ± 0.001	0.427 ± 0.016	0.492 ± 0.001	0.24 ± 0.02
0.40	298.8 ± 0.3	0.250 ± 0.012	0.340 ± 0.001	0.086 ± 0.012	0.413 ± 0.001	0.18 ± 0.05
0.40	326.1 ± 0.3	0.479 ± 0.012	0.250 ± 0.001	0.236 ± 0.013	0.340 ± 0.001	0.22 ± 0.02
0.40	345.3 ± 0.3	0.768 ± 0.012	0.258 ± 0.001	0.425 ± 0.013	0.340 ± 0.001	0.15 ± 0.01
0.20	298.7 ± 0.3	0.233 ± 0.012	0.156 ± 0.001	0.085 ± 0.015	0.185 ± 0.001	0.09 ± 0.03
0.20	326.2 ± 0.3	0.392 ± 0.012	0.116 ± 0.001	0.218 ± 0.015	0.156 ± 0.001	0.06 ± 0.01
0.20	345.4 ± 0.3	0.596 ± 0.012	0.092 ± 0.001	0.390 ± 0.015	0.149 ± 0.001	0.02 ± 0.01

Relative standard uncertainty u_r are $u_r(y^{\text{CO}_2\text{i}}) = 0.02$, $u_r(y^{\text{CO}_2\text{ind}}) = 0.003$, $u_r(y^{\text{CO}_2\text{eq}}) = 0.003$.

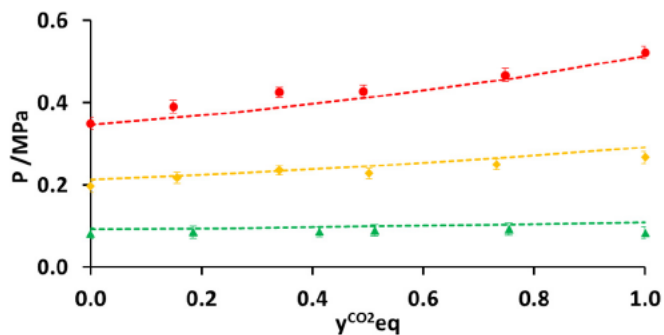


Fig. 4. Clathrate equilibrium pressure as a function of the equilibrium CO_2 mole fraction in the gas phase at 344 K (red), 325 K (yellow) and 298 K (green). Symbols: experimental data. Dashed line: modeled data using the Conde et al. model [11]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

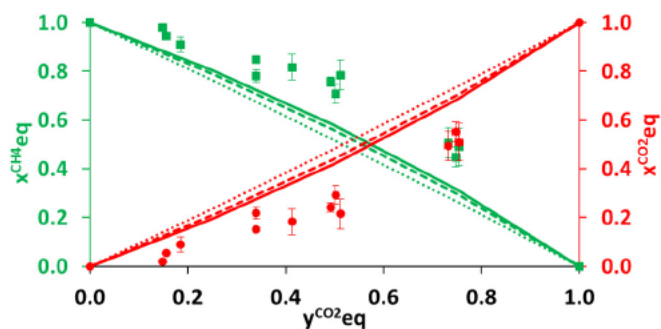


Fig. 5. Clathrate composition in CO_2 (red) and CH_4 (green) at the equilibrium clathrate forming conditions as a function of the equilibrium CO_2 mole fraction in the gas phase. Experimental data: (●) CO_2 and (■) CH_4 . Modeled data using the Conde et al. model [11]: (solid line) 344 K, (dashed line) 325 K and (dotted line) 298 K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

reproduced. Actually, the modeled occupancy at 298 K for CH_4 in the HQ clathrate is 0.37 which is in very good agreement with the experimental value of 0.399 ± 0.032 , whereas the modeled occupancy for CO_2 at the same temperature is 0.42 and the experimental one is 0.538 ± 0.031 .

Using Eqs. (1) and (2), the CO_2 capture selectivities are calculated from the molar compositions of the CO_2/CH_4 gas mixture in the clathrate and in the gas phase; the results are shown in Fig. 6. The obtained selectivity values are always found to be less than 1 at equilibrium conditions for the entire compositional range. In fact, the experimental selectivity fluctuates between 0.14 and 0.56. The selectivities predicted using Conde's model (values from 0.72 to 0.93) are found to be higher than the experimental values at the same conditions. However, as in the experiments, the model demonstrates that at equilibrium conditions CH_4 molecules are preferentially captured from the CO_2/CH_4 mixtures. In a practical point of view, the selective capture of CO_2 from a CO_2/CH_4 mixture by HQ clathrate formation cannot be performed close to the equilibrium line. As demonstrated recently in a previous work [17], higher selectivity toward CO_2 can be obtained either by working far from the equilibrium conditions (e.g. at 323 K 3.0 MPa) or by contacting the gas mixture to the "guest free" HQ clathrate formed initially by using CO_2 .

Finally, it is interesting to note that the clathrate compositions obtained at equilibrium are much lower than those reported by Lee and coworkers [3], who obtained a CO_2 mole fraction of 0.97 in the clathrate (i.e. molar ratio of $29 \text{ mol}^{\text{CO}_2}/\text{mol}^{\text{CH}_4}$) from an equimolar CO_2/CH_4 gas mixture. Unfortunately, they do not provide any infor

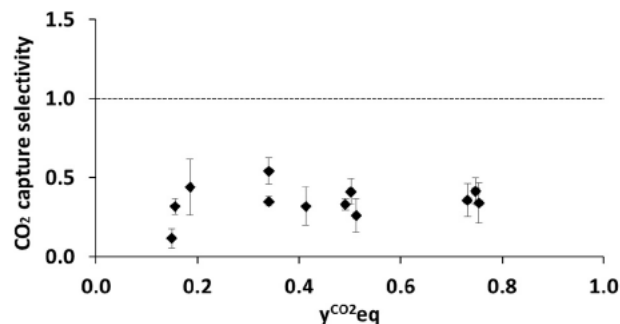


Fig. 6. CO_2 capture selectivity at equilibrium versus the equilibrium CO_2 mole fraction in the gas phase.

mation on the pressure and temperature conditions in their experiment. In comparison, we found that the gas with a CO_2 mole fraction of 0.50 is at equilibrium with a mixed HQ clathrate and a CO_2 mole fraction of 0.29 (i.e. molar ratio of $0.4 \text{ mol}^{\text{CO}_2}/\text{mol}^{\text{CH}_4}$) at 0.229 MPa and 323.7 K. This difference could be ascribed to specific experimental conditions: (i) Lee and coworkers used the metastable guest free β HQ intermediate for contacting the CO_2/CH_4 gas mixture, whereas we started the reaction with α HQ in the thermodynamic experiments and (ii) as the operating conditions considered by Lee et al. [3] are not known, we believe that their operating point is far from the equilibrium data lines determined in this work. Accordingly, the clathrate composition obtained out of equilibrium may be very different to the values found in the three phase equilibrium conditions. Ongoing experimental and modeling work is currently being conducted in our laboratory to study and characterize these inclusion compounds out of their thermodynamic equilibrium conditions.

5. Conclusions

In this work we studied the equilibrium conditions of CO_2/CH_4 mixed HQ clathrates in temperatures ranging from about 298 to 343 K, and obtained thermodynamic data for the first time. The clathrate equilibrium curves obtained from all investigated CO_2/CH_4 mixtures are, as expected, found to be between those of pure CH_4 HQ and pure CO_2 -HQ clathrates.

With gas compositions enclosed in these HQ clathrates determined by mass balance, the CO_2 capture selectivity is found to be less than 1 at the clathrate forming conditions. These data imply that the CH_4 molecules are preferentially captured from the CO_2/CH_4 mixtures by HQ clathrates at equilibrium conditions.

The comparison of experimental data with data computed using the Conde et al. model gives a very good agreement in terms of clathrate phase equilibria. Nevertheless, the modeling does not perfectly predict the clathrate occupancies and as a result the selectivity is overestimated.

For a practical point of view to propose efficient CO_2 capture processes, additional work is necessary to examine how the selectivity varies for various operating conditions. Such experiments are currently in progress in our laboratory.

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