HAL
open science

Phase equilibrium properties of CO 2 /CH 4 mixed gas hydroquinone clathrates: Experimental data and model predictions

Romuald Coupan, Maria Martin Conde, Christelle Miqueu, Christophe Dicharry, Jean-Philippe Torré

To cite this version:

Romuald Coupan, Maria Martin Conde, Christelle Miqueu, Christophe Dicharry, Jean-Philippe Torré. Phase equilibrium properties of CO 2 /CH 4 mixed gas hydroquinone clathrates: Experimental data and model predictions. Journal of Chemical Thermodynamics, 2018, 116, pp.230-234. 10.1016/j.jct.2017.09.021 . hal-01987925

HAL Id: hal-01987925

https://hal.science/hal-01987925v1

Submitted on 21 Jan 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Open Archive Toulouse Archive Ouverte

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible

This is an author's version published in: http://oatao.univ-toulouse.fr/21613

Official URL: https://doi.org/10.1016/j.jct.2017.09.021

To cite this version:

Coupan, Romuald and Conde, Maria Martin and Miqueu, Christelle and Dicharry, Christophe and Torré, Jean-Philippe *Phase equilibrium properties of CO 2 /CH 4 mixed gas hydroquinone clathrates: Experimental data and model predictions.* (2018) The Journal of Chemical Thermodynamics, 116. 230-234. ISSN 0021-9614

Any correspondence concerning this service should be sent to the repository administrator: tech-oatao@listes-diff.inp-toulouse.fr

Phase equilibrium properties of CO_2/CH_4 mixed gas hydroquinone clathrates: Experimental data and model predictions

Romuald Coupan [a], Maria Martin Conde [a,b], Christelle Miqueu [c], Christophe Dicharry [a], Jean-Philippe Torré [a,*]

[a] CNRS/TOTAL/UNIV PAU & PAYS ADOUR, Laboratoire des Fluides complexes et leurs Réservoirs-IPRA, UMR5150, 64000 PAU, France
[b] UNIVERSITÀ ROMA TRE, Dipartimento di Matematica e Fisica, Via della Vasca Navale 84, 00146 Roma, Italy
[c] CNRS/TOTAL/UNIV PAU & PAYS ADOUR, Laboratoire des Fluides complexes et leurs Réservoirs-IPRA, UMR5150, 64600 Anglet, France

A B S T R A C T

Hydroquinone (HQ) clathrates seem to be promising inclusion compounds for selective CO_2 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 CO_2/CH_4 gas mixtures. The clathrate composition is given for each equilibrium point. The capture selectivity is calculated from the molar composition of the CO_2/CH_4 gas mixture in the clath rate and in the gas phase. The results obtained reveal that CH_4 molecules in the CO_2/CH_4 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 CO_2, CH_4, and N_2 in well specified thermody namic conditions of temperature and pressure [1]. Gaseous mole cules (called "guests") are encaged inside a molecular network formed by HQ molecules (called "hosts"). Clathrates containing dif ferent 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 CO_2 from a CO_2/CH_4 gas mix ture is particularly important in the areas of energy, the environ ment 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], CO_2 [10], CH_4 [10] and N_2 [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 engineer ing data for process design. Therefore, this study presents, for the first time, equilibrium curves of mixed gas HQ clathrates. Equilib rium data are obtained from isothermal titration experiments [10], in the temperature range of 298 343 K for HQ clathrates formed with CO_2/CH_4 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 exper iments. CO_2/CH_4 gas mixtures with CO_2 mole fractions of 0.2, 0.4, 0.6 and 0.8 (minimum mole fraction purity of 99.995%) were pur chased 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 ±2%. The speci fications of the chemicals used in this study are also given in Table 1.

* Corresponding author.
E-mail address: jean-philippe.torre@univ-pau.fr (J.-P. Torré).

https://doi.org/10.1016/j.jct.2017.09.021 .

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 Coupan and coworkers [10] in experiments to obtain the phase equilibria and clathrate occupancies of CO_2 , CH_4 and N_2 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 pres sure 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 measure ments is ±0.2 K and ±0.01 MPa, respectively. Refer to [10] for tech nical 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 con centration of 572 ± 5 $g^{HQ}/l^{Solvent}$ (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 sys tem 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

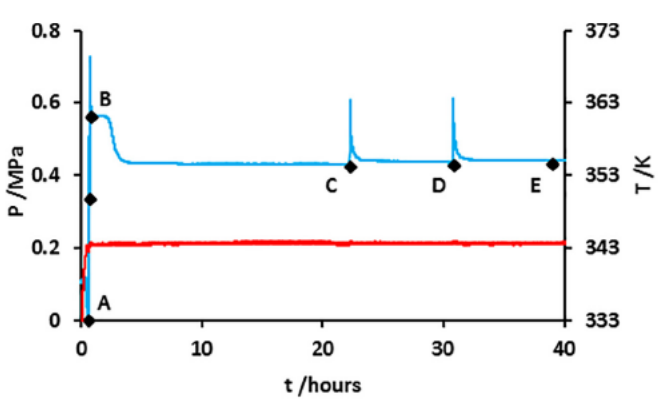

Fig. 1. Example for isothermal titration: (blue line) vapor pressure of the CO_2/CH_4 mixture; ◆, equilibrium vapor pressure of the CO_2/CH_4 mixture; (red line) temperature, as a function of time. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

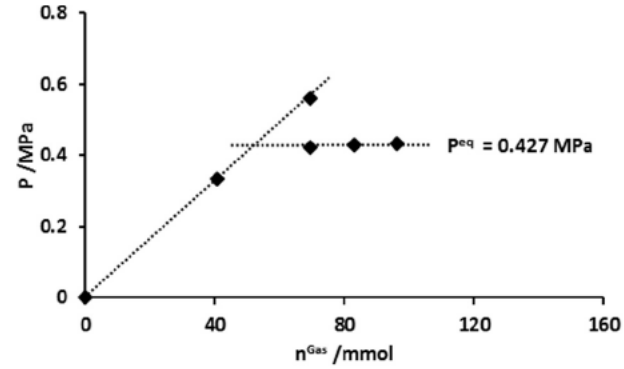

Fig. 2. Example of isothermal titration at 343.7 K: Vapor pressure of CO_2/CH_4 mixture versus the amount of CO_2/CH_4 gas mixture added to the reactor with HQ and butyl acetate load.

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 equilib rium 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):

$$n^{i}_{clathrate} \quad n^{i}_{gas}\Big|_{t_{ind}} \quad n^{i}_{gas}\Big|_{t_{eq}} \quad \frac{y^{i}PV}{zRT}\Big|_{t_{ind}} \quad \frac{y^{i}PV}{zRT}\Big|_{t_{eq}} \tag{1}$$

where the superscript i corresponds to the CO_2 or CH_4 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 pres sure, 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 clath rate composition can be obtained by the ratio of the molar quantity of one of the constituents to the total quantity. The CO_2 capture selectivity (also termed the "separation factor" in literature [13]) in the clathrate forming conditions can be obtained from Eq. (2):

$$S.F.^{CO2/CH4} \quad \frac{x^{CO2}/(1 \quad x^{CO2})}{y^{CO2}/(1 \quad y^{CO2})} \tag{2}$$

where x^{CO2} and y^{CO2} are the CO_2 molar compositions in the CO_2/CH_4 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 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:

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

and

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

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 CO_2/CH_4 gas mixtures of initial CO_2 mole fractions equal to 0.2, 0.4, 0.6 and 0.8. The obtained clathrate equilibrium points are associated with equilibrium CO_2 mole fractions ranging from 0.15 to 0.75. The experimental equilibrium data and the gas composition before reaction for the different CO_2/CH_4 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] CO_2 and CH_4 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 CH_4 HQ and CO_2 HQ systems. We can see that the equilibrium points associated with high CO_2 mole fractions are very close to the CO_2 HQ equilibrium curve and the contrary for equilibrium points associated with high CH_4 mole fractions. It is worth noting that the same observations are made for clathrate hydrates formed from the CO_2/CH_4 gas mixtures [14].

Additionally, our equilibrium data for CO_2/CH_4 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 CO_2 and CH_4 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

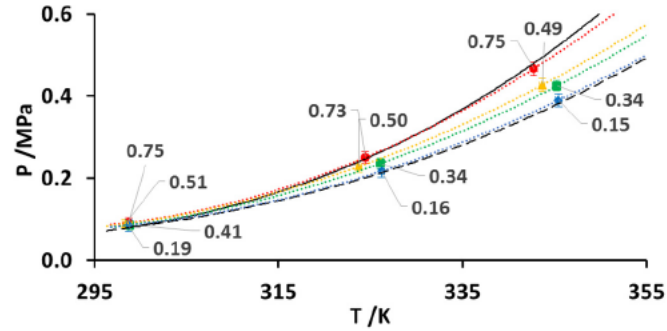

Fig. 3. Clathrate equilibrium pressure as a function of temperature for CO_2/CH_4 mixed-gas HQ clathrates for initial CO_2 mole fractions of 0.2 (blue), 0.4 (green), 0.6 (yellow) and 0.8 (red). Data labels indicate the equilibrium CO_2 mole fraction in the gas phase after the reaction. Equilibrium curve for pure components [10]: CO_2 (full line) and CH_4 (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 CH_4 and N_2 (e.g. same 3.95 Å diameter cavity). The Lennard Jones parameter set for CO_2 (i.e. σ = 4.416 Å and ε/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 CO_2 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 CO_2/CH_4 mixed HQ clathrates whereas the model does not consider the atypical behavior of CO_2 cavities (e.g. the CO_2 distorts the HQ clathrate cavities [16]). It is worth noting that the agreement is also fairly good for pure CO_2 (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 CO_2 mole fraction in the clathrate increases with increasing CO_2 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 CH_4 in the clathrate. This is not surprising as the Conde et al. model [11] underestimates the occupancy of the pure CO_2 HQ clathrate whereas the occupancy of the pure CH_4 HQ clathrate is perfectly

Table 2
Equilibrium points of CO_2/CH_4-HQ clathrates obtained by isothermal titration: ($y^{CO2}i$) molar composition of the initial gas mixture, (T) temperature; Variables before reaction at the induction time: (y_{ind}^{CO2}) molar composition of the gas mixture, and (P_{ind}) induction pressure; Variables after reaction at equilibrium state: (y_{eq}^{CO2}) molar composition of the gas mixture in the gas phase, (x_{eq}^{CO2}) molar composition of the gas mixture in the clathrate phase, and (P_{eq}) equilibrium pressure.

		Before Reaction (at induction time)		After Reaction (at equilibrium)		
$y^{CO2}i$	T /K	P_{ind}/MPa	y_{ind}^{CO2}	P_{eq}/MPa	y_{eq}^{CO2}	x_{eq}^{CO2}
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 $u_r(y^{CO2}i)$ = 0.02, $u_r(y^{CO2}ind)$ = 0.003, $u_r(y^{CO2}eq)$ = 0.003.

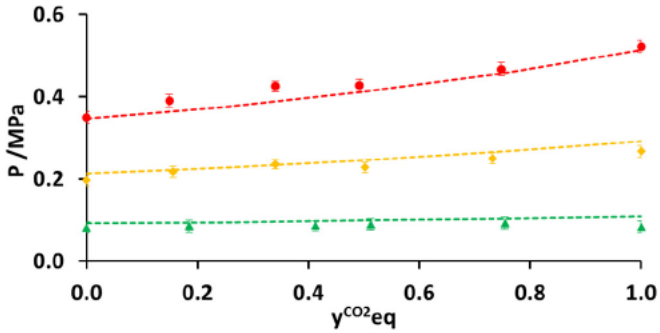

Fig. 4. Clathrate equilibrium pressure as a function of the equilibrium CO_2 mole fraction in the gas phase at 344 K (red), 325 K (yellow) and 298 K (green). Symbols: experimental data. Dashed line: modeled data using the Conde et al. model [11]. (For interpretation of the references to color in this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

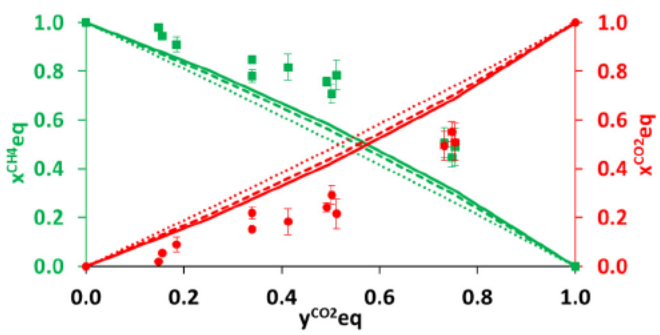

Fig. 5. Clathrate composition in CO_2 (red) and CH_4 (green) at the equilibrium clathrate forming conditions as a function of the equilibrium CO_2 mole fraction in the gas phase. Experimental data: (●) CO_2 and (■) CH_4. Modeled data using the Conde et al. model [11]: (solid line) 344 K, (dashed line) 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 mol^{CO2}/mol^{CH4}) from an equimolar CO_2/CH_4 gas mixture. Unfortunately, they do not provide any information 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 mol^{CO2}/mol^{CH4}) 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.

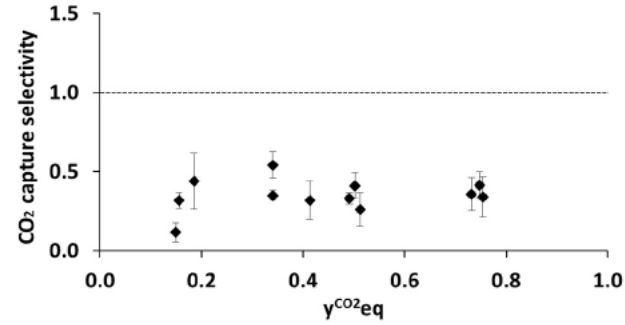

Fig. 6. CO_2 capture selectivity at equilibrium versus the equilibrium CO_2 mole fraction in the gas phase.

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.

Acknowledgments

The authors wish to thank the entire work group involved in the ORCHIDS project. Total E&P, and particularly the "Gas Solutions" department is acknowledged for financial contribution. We also thank J. Diaz for technical assistance and the Carnot Institute ISIFoR for supporting the project.

References

[1] J.L. Atwood, J.W. Steed, Encyclopedia of Supramolecular Chemistry, CRC Press Taylor & Francis Group, Boca Raton, 2004.

[2] J.-W. Lee, J.-H. Yoon, Preferential occupation of CO_2 molecules in hydroquinone clathrates formed from CO_2/N_2 gas mixtures, J. Phys. Chem. C 115 (2011) 22647–22651.

[3] Y.-J. Lee, K.W. Han, J.S. Jang, T.-I. Jeon, J. Park, T. Kawamura, Y. Yamamoto, T. Sugahara, T. Vogt, J.-W. Lee, Selective CO_2 trapping in guest-free hydroquinone clathrate prepared by gas phase synthesis, Chem. Phys. Chem. 12 (2011) 1056–1059.

[4] J.-W. Lee, S.-P. Kang, J.-H. Yoon, Highly selective enclathration of ethylene from gas mixtures, J. Phys. Chem. C 118 (2014) 6059–6063.

[5] J.-W. Lee, S.-P. Kang, J.-H. Yoon, Competing occupation of guest molecules in hydroquinone clathrates formed from binary C_2H_4 and CH_4 gas mixtures, J. Phys. Chem. C 118 (2014) 7705–7709.

[6] J.-W. Lee, P. Dotel, J. Park, J.-H. Yoon, Separation of CO_2 from flue gases using hydroquinone clathrate compounds, Korean J. Chem. Eng. 12 (2015) 2507–2511.

[7] J.-W. Lee, J. Poudel, M. Cha, S.J. Yoon, J.-H. Yoon, Highly selective CO_2 extraction from a mixture of CO_2 and H_2 gases using hydroquinone clathrates, Energy Fuels 30 (2016) 7604–7609.

[8] Y.N. Kazankin, A.A. Palladiev, A.M. Trofimov, Study of heterogeneous equilibria for noble gas - HQ clathrate systems. Part I: phase diagrams, Zh. Obshch. Khim 42 (1972) 2607–2611.

[9] Y.N. Kazankin, A.A. Palladiev, A.M. Trofimov, Study of heterogeneous equilibria for noble gas – HQ clathrate systems. Part II: clathration isotherms, Zh. Obshch. Khim 42 (1972) 2611–2615.

[10] R. Coupan, M. Chabod, C. Dicharry, J. Diaz, C. Miqueu, J.-P. Torré, Experimental determination of phase equilibria and occupancies for CO_2, CH , and N_2 hydroquinone clathrates, J. Chem. Eng. Data 61 (2016) 2565–2572.

4

[11] M.M. Conde, J.P. Torré, C. Miqueu, Revisiting the thermodynamic modeling of type I gas-hydroquinone clathrates, Phys. Chem. Chem. Phys. 18 (2016) 10018–10027.

[12] A. Kordas, K. Tsoutsouras, S. Stamataki, D. Tassios, A generalized correlation for the interaction coefficients of CO_2-hydrocarbon binary mixtures, Fluid Phase Equilibria 93 (1994) 141–166.

[13] P. Linga, R. Kumar, P. Englezos, The clathrate hydrate process for post and pre-combustion capture of carbon dioxide, J. Hazardous Mater. 149 (2007) 625–629.

[14] S. Adisasmito, R.J. Frank, E.D. Sloan, Hydrates of Carbon Dioxide and Methane Mixtures, J. Chem. Eng. Data 36 (1991) 68–71.

[15] L.S. Tee, S. Gotoh, W.E. Stewart, Molecular parameters for normal fluids: The Lennard-Jones 12–6 potential, I&EC Fundam. 5 (1966) 356–363.

[16] H.G. McAdie, Thermal decomposition of molecular complexes: IV. Further studies of the β-quinol clathrates, Can. J. Chem. 44 (1966) 1373–1386.

[17] R. Coupan, E. Péré, C. Dicharry, J.-P. Torré, New insights on gas hydroquinone clathrates using in situ Raman spectroscopy: formation/dissociation mechanisms, kinetics, and capture selectivity, J. Phys. Chem. A 121 (2017) 5450–5458.