An Experimental and Theoretical Study of CO2 Hydrate Formation Systems

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An Experimental and Theoretical Study of CO₂ Hydrate Formation Systems

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CERE
Center for Energy Resources Engineering
Prolegomenon

At first, the author would like to express his gratitude to his parents, his brother and our Father in Heaven for his existence and providence during his life. In Appendix E the summary of his PhD study is shown.

Secondly, the author would like to thank his main supervisor Georgios Kontogeorgis for giving him the chance to work on this project and his support and Nicolas von Solms for his fruitful comments especially at the early stages of this PhD.

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In addition, warm thanks belong to his colleagues, Alay, Martin and Xiaodong, for their guidance and discussion of the modeling part of this work.


…and in France, Stefano, Martha, Anne, Jie, Marine, Jamal, Lydia, f.Panayiotis, Jocelyne, Hervé.

ὁ Θεὸς ἀγάπη ἐστί, καὶ ὁ μένων ἐν τῇ ἁγάπῃ ἐν τῷ Θεῷ μένει καὶ ὁ Θεὸς ἐν αὐτῷ.\textsuperscript{a}

A΄ Ἰωάν. 4, 16

\textsuperscript{a} God is love, and the one that stays in His love, God stays in him.

A John 4, 16
Synopsis

Synopsis in English

Hydrate crystallization can become equally important carbon capture method provided that this technology undergoes further research. Toward this objective, this study tries to shed light on a quite new topic of research: hydrate promotion. Hydrate promotion implies the production of hydrate at lower pressures (and thus lower adjunctive capital/operational costs) by the use of special chemicals (promoters).

At first, extensive literature review has shown that both experimental data and modeling in this subject are imperative. Therefore, experimental data were produced and published (see Appendix E) using as promoters tetra-n-butyl ammonium salts of bromide, fluoride and cyclopentane in collaboration with MINESParisTech in France. These chemicals are well known for their reduction capabilities of hydrate formation pressure. The results are in good accordance with the literature. Moreover, the simultaneous combination of these chemicals achieved greater pressure reduction than if they were used separately. Then, experimental uncertainties were measured (for pressure/temperature transducers and gas chromatograph) and calculated (for the inserted quantities of water and chemicals). The uncertainties were at an acceptable level for all cases. A further evaluation of the experimental data, regarding their consistency, included the use of Clapeyron equation. It was shown that the results of this work and many of the systems from literature are quite satisfactory. Finally, the well-known van der Waals-Platteeuw hydrate model coupled with CPA EoS was used against experimental data as it was developed in CERE, DTU. The model predicted very satisfactory the CP results of this work and also other CO₂+cyclolkane hydrate results from literature. This model’s consistency lies inter alia on the ground that fluid phases were modeled only with CPA EoS while correlations are utilized in current publications for the aqueous phase and an EoS for the hydrate phase.
Synopsis på Dansk


Σύνοψις

Ἡ κρυσταλλοποίησης διὰ υδριτῶν βαθμηδὸν δύναται περικυδῆς μέθοδος εἶναι δέσμευσης τοῦ διοξειδίου τοῦ ἄνθρακος υπό τὴν αἱρέσιν ὅτι ἡ τεχνικὴ αὕτη ὑπόκειται εἰς περαιτέρων ἔρευναν. Πρὸς τοῦτον τὸν στόχον, ἡ διατριβή αὕτη πραγματεύεται περὶ πνος νέου θέματος ὃ καλεῖται υδριτικὴ προώθησις. Ὡς υδριτικὴ προώθησις συνιέναι δεῖ τὴν παραγωγὴν υδριτῶν εἰς ἦττον πιέσεις καὶ τοιουτοτόπως μείονας παρεπόμενας λειτουργικὰς ἐξόδους διὰ τῆς χρήσεως εἰδικῶν χημικῶν ουσιῶν: τῶν προωθητῶν.

Ἐν ἀρχῇ, ἀμα τῇ τῆς υπαρχοῦσης βιβλιογραφίας διεξοδικὴ ἔρευναν ἔγεντο ὅτι πειραματικὰ δεδομένα καὶ ἄλγοριθμοποίησις ἐλλείπῃ. Κατὰ συνέπειαν, νέα πειραματικὰ δεδομένα παρηγάγοντο καὶ ἐδημοσιεύθησαν ὑπὸ τῆς χρήσεως τέτρα-ν-βουτυλαμμωνιακῶν ἁλάτων τε κυκλοπεντανίου συνεργείᾳ τῆς ἐν Κυανῂ Πηγῂ ἐν Φραγκίᾳ Ἐθνικῆς Σχολῆς Μεταλλολόγων. Τοιαῦται οὐσίαι γνώριμαι εἰσὶ πρὸς τὰς δυνατότητας μείωσης σχηματισμοῦ υδριτῶν. Τὰ ἀποτελέσματα συνάδουσι καλῶς τῇ υπαρχοῦσῃ βιβλιογραφίᾳ. Ἐπὶ δὲ ὁ κατ’ ἀμφοὺς συνδυασμὸς τῶν προωθητῶν ἐπήνεγκεν μειοτέρων πτῶσιν πιέσεως ὡς ἄν μονόθεν χρησιμοποιοῖντο. Κατόπιν, πειραματικὰ διακυμάνσεις ἐμετρήθησαν τοῖς μετρηταῖς πιέσεως καὶ θερμοκρασίας καὶ ὑπολογίσθησαν τοῖς εἰσαχθείσασι μεγέθεσι ὑδάτων καὶ χημικῶν ουσιῶν.
List of Abbreviations

CC6  cyclohexane  
CC7  cycloheptane  
CC8  cyclooctane  
CP  cyclopentane  
CPA  Cubic-Plus-Association equation of state  
DTAC  dodecyl trimethyl ammonium chloride  
EC  equilibrium cell  
EoS  equation of state  
GC  gas chromatograph  
mCC6  methyl-cyclohexane  
mCP  methyl-cyclopentane  
SAFT  statistical associating fluid theory  
SDS  sodium dodecyl sulfate  
SRK  Soave-Redlich-Kwong equation of state  
rpm  rounds per minute  
TBAB  tetra-n-butyl ammonium bromide  
TBAC  tetra-n-butyl ammonium chloride  
TBAF  tetra-n-butyl ammonium fluoride  
TBANO3  tetra-n-butyl ammonium nitrate  
TBPB  tetra-n-butyl phosphonium bromide  
THF  tetrahydrofuran  

List of Symbols

\( a_0 \)  pure component parameter of CPA/SRK EoS  \([\text{Pa} \cdot \text{m}^6 \cdot \text{mol}^{-2}]\)  
\( b \)  pure component parameter of CPA/SRK EoS  \([\text{m}^3 \cdot \text{mol}^{-1}]\)  
\( c_1 \)  pure component parameter of CPA/SRK EoS  [-]  
\( C(T) \)  Langmuir constant  [-]  
\( f(T,P,y) \)  fugacity  [-]  
\( g(V_m) \)  radial distribution function in CPA  [-]  
\( \Delta H \)  (apparent) dissociation enthalpy  \([\text{kJ} \cdot \text{mol}^{-1}]\)  
\( k_B \)  Boltzmann constant  \([\text{J} \cdot \text{K}^{-1}]\)  
\( k_{ij} \)  interaction parameter in CPA EoS  [-]  
\( n \)  quantity of gas inserted in equilibrium cell  \([\text{mol}]\)  
\( P \)  hydrate equilibrium pressure  \([\text{MPa}]\)  
\( P_R \)  reference hydrate dissociation pressure  \([\text{MPa}]\)  
\( R^2 \)  coefficient of determination  [-]  
\( R_m \)  radius of cavity type \( m \)  \([\text{m}]\)  
\( r \)  linear distance from centre of the cell  \([\text{m}]\)  
\( T \)  hydrate equilibrium temperature  \([\text{K}]\)  
\( u(T) \)  temperature error  \([\text{K}]\)
List of Abbreviations and Symbols

\[ u(P) \] pressure error \[ \text{[Bar]} \]
\[ U(T) \] standard temperature uncertainty \[ \text{[K]} \]
\[ U(P) \] standard pressure uncertainty \[ \text{[Bar]} \]
\[ U(y) \] standard uncertainty of gas in gas mixture cylinder \[ \text{[mol\%]} \]
\[ U(n) \] standard uncertainty of gas molar composition in EC \[ \text{[mol\%]} \]
\[ u_{cal.}(y) \] calibration error of gas in gas mixture cylinder \[ \text{[mol\%]} \]
\[ w \] spherical core cell potential \[ \text{[m]} \]
\[ x \] liquid phase composition \[ \text{[mol\%]} \]
\[ Y \] water-free composition \[ \text{[mol\%]} \]
\[ y \] vapour phase mole fraction \[ \text{[mol\%]} \]
\[ Z \] compressibility factor \[ \text{[-]} \]
\[ Z_m \] coordination number for the guest molecule \[ \text{[-]} \]

Greek letters

\[ \beta \] is referred to empty hydrate lattice (meta-stable \( \beta \)-phase)
\[ \beta_{ABij} \] association volume
\[ \gamma \] symmetric activity coefficient
\[ \Delta_{ABij} \] association strength in CPA EoS
\[ \varepsilon \] characteristic energy (is referred to cell potential)
\[ \varepsilon_{ABij} \] association energy
\[ \theta \] fractional occupancy
\[ \nu \] number of cavities
\[ \varphi \] fugacity coefficient
\[ \kappa \] binary interaction parameter
\[ \mu \] chemical potential
\[ \rho \] gas density
\[ \omega \] acentric factor

Superscripts or subscripts

\[ \text{cal.} \] calibration
\[ H \] hydrate phase
\[ m \] cavity type
\[ ij \] components \( i \) and \( j \)
\[ \text{diss.} \] dissociation
\[ \text{rep.} \] repeatability
\[ w \] liquid or ice rich phase
\[ 0 \] reference state (273.15 K and 1 atm)
\[ * \] pure phase
List of Tables

Table 2.1 Gas hydrate main structures and main physical description

Table 2.2 Experimental Observations on the “Memory Effect” Phenomenon

Table 2.3 Hydrate dissociation procedures

Table 2.4 Most common techniques for macroscopic hydrate measuring

Table 2.5 Most common techniques for microscopic hydrate measuring

Table 2.6 Techniques presented according to their measuring capabilities

Table 3.1 Temperature and pressure parameters as came out from calibration

Table 3.2 Polynomial expression composition parameters as came out from calibration for CO₂ and N₂

Table 3.3 Chemicals used in this work

Table 4.1 Gas mixtures composition uncertainties

Table 4.2 Coefficient of determination of ΔHₐ₅₆ (kJ/mol) in terms of temperature for TBAB and TBAB+CP systems of this work including TBAB literature

Table 4.3 Coefficient of determination of ΔHₐ₅₆ in terms of temperature for systems with CP hydrates

Table 4.4 Coefficient of determination (R²) of ΔHₐ₅₆ (kJ/mol) in terms of temperature for systems of this work including TBAF literature

Table 5.1 Water lattice and unit cell parameters for the van der Waals-Platteeuw hydrate model

Table 5.2 Thermodynamic properties for the reference hydrate in the van der Waals-Platteeuw hydrate model

Table 5.3 Kihara cell potential parameters used in this work

Table 5.4 Cubic-Plus-Association (CPA) equation of state pure component parameters and association schemes

Table 5.5 Interaction parameters (kij) for all binary pairs used in this work

Table 5.6 Adjusted parameters for all binary pairs used in qCPA

Table 5.7 The average absolute deviation for pressure of every system of this work

Table A.1 Experimental studies for gas hydrates of CO₂+gas/gas mixture systems+H₂O

Table A.2 Experimental studies on clathrate/semi-clathrate hydrate for CO₂ + gas/gases systems+promoters

Table B.1 Hydrate equilibrium points for CP and TBAB+CP solutions with temperature and pressure uncertainties
List of Tables

Table B.2  Hydrate equilibrium points for TBAB solution with temperature and pressure uncertainties ..........................................................129

Table B.3  Hydrate equilibrium points for TBAF solution with temperature and pressure uncertainties ..................................................................................................................130

Table B.4  Gas molar composition and gas inserted uncertainty $U(n_{gas})$ for every hydrate equilibrium point .........................................................131

Table C.1  Most recent modeling approaches in hydrate phase equilibria ........................................................................................................133

Table D.1  Kihara parameters for the compounds examined in this work .................................................................................................142
List of Figures

Figure 1.1 Carbon capture methods\(^{18}\) .................................................................................................. 3
Figure 2.1 Gas Hydrate main structures: (a) pentagonal dodecahedron (5\(^{12}\)), (b) tetrahecahedron (5\(^{12}\)6\(^{2}\)), (c) hexahecahedron (5\(^{12}\)6\(^{2}\)), (d) irregular dodecahedron (4\(^{5}\)5\(^{6}\)) and (e) icosahedron (5\(^{12}\)6\(^{2}\))\(^{24}\) ........................................ 8
Figure 2.2 Semi-clathrate structure of TBAB\(^{28}\) ................................................................................ 9
Figure 2.3 Hydrate loci for several NG components. The designations are: \(L_w \equiv H_2O\), \(V \equiv \) vapor, \(I \equiv \) ice, \(H \equiv \) hydrate, \(\text{and } L_{nc} \equiv \) non aqueous liquid\(^{24}\) .......................... 11
Figure 2.4 Temperature and pressure trace for determination of equilibrium point of \(\text{CO}_2-\text{H}_2\) (40:60) mixture gas hydrate systems with TBAB additives at initial temperature of 293.15 K and pressure of 0.99 MPa\(^{37}\) ....................................................... 16
Figure 2.5 Schematic diagram of high pressure visual autoclave cell\(^{80}\) ............................................ 17
Figure 2.6 Rocking cell apparatus\(^{24}\) .................................................................................................. 17
Figure 2.7 Quartz crystal microbalance apparatus\(^{59}\) ................................................................. 17
Figure 2.8 DSC device: R, reference vessel; M, sample vessel\(^{61}\) ..................................................... 17
Figure 2.9 Equilibrium hydrate formation conditions for \(\text{CO}_2/\text{H}_2\) mixture using THF\(^{111}\) .................. 21
Figure 2.10 Phase equilibrium conditions for \(\text{CO}_2 + \text{H}_2\text{O}\) and \(\text{CO}_2 + \text{TBAB} + \text{H}_2\text{O}\).
\(\text{CO}_2 + \text{H}_2\text{O}: \bullet, \text{Li et al.}^{104}; \circ, \text{Adisasmito et al.}^{117}. \text{CO}_2 + \text{TBAB} + \text{H}_2\text{O}:
\(\bigcirc, 2.93 \text{ mol\%}, \text{Li et al.}^{104}; \blacklozenge, 6.17 \text{ mol\%}, \text{Li et al.}^{104}; \blackdiamondsuit, 2.58 \text{ mol\%}, \text{Lin et al.}^{118}; \blacklozenge, 5.51 \text{ mol\%}, \text{Lin et al.}^{118}; \star, 2.90 \text{ mol\%}, \text{Duc et al.}^{9}; \blackstar, 6.10 \text{ mol\%}, \text{Duc et al.}^{9}\) ........................................ 22
Figure 2.11 Phase equilibrium conditions for the \(\text{CO}_2 + \text{H}_2\text{O}\) and \(\text{CO}_2 + \text{TBAB} + \text{H}_2\text{O}\).
\(\text{CO}_2 + \text{H}_2\text{O}: \bullet, \text{Li et al.}^{104}; \circ, \text{Adisasmito et al.}^{117}. \text{CO}_2 + \text{TBAB} + \text{H}_2\text{O}:
\(\bigcirc, 2.93 \text{ mol\%}; \blacklozenge, 6.17 \text{ mol\%}, \text{Li et al.}^{104}\) .................................................................................. 22
Figure 2.12 Phase equilibrium conditions for the \(\text{CO}_2 + \text{water and CO}_2 + \text{TBAC} + \text{H}_2\text{O}\).
\(\text{CO}_2 + \text{H}_2\text{O}: \bullet, \text{Li et al.}^{104}; \circ, \text{Adisasmito et al.}^{117}. \text{CO}_2 + \text{TBAC} + \text{H}_2\text{O}:
\(\bigcirc, 2.93 \text{ mol\%}; \blacklozenge, 6.17 \text{ mol\%}, \text{Li et al.}^{104}\) ........................................................................... 22
Figure 2.13 Hydrate phase equilibrium\(^{120}\) for the gas mixture containing mol fraction
0.392 \(\text{CO}_2\), 0.608 \(\text{H}_2\) and the ternary gas mixture containing mol faction
0.381 \(\text{CO}_2\), 0.594 \(\text{H}_2\) and 0.025 \(\text{C}_3\text{H}_8\) .......................................................................................... 23
Figure 2.14 \(\text{CO}_2\) pressure, \(P_{\text{CO}_2}\), versus temperature, \(T\), \(H-L-V\) equilibrium data for
the systems \(\text{CO}_2+\text{H}_2\text{O}\)\(^{16,122}\) and \(\text{CO}_2+\text{TBPB}+\text{H}_2\text{O}\)\(^{121}\) ............................................................... 24
Figure 2.15 Four-phase (\(\text{H}_2\text{O}-\text{L}_w-L_r-V\)) equilibrium pressures (absolute) as functions of
temperature for mixed hydrates of CP/THF/\(\text{CO}_2\). hydrates formed from
a two-liquid phase system prepared from an aqueous solution containing
4 wt\% THF and an organic phase containing pure CP. For comparison,
(H-L\(_w\)-L\(_r\)-V) hydrate equilibrium data exhibiting a mixed CP/CO\(_2\) hydrate phase
of the ternary system \{H\(_2\)O + CP + CO\(_2\)\} are included. The initial vapor phase
consists of pure CO\(_2\) in both cases. (\(\bullet\) ) CP/THF/CO\(_2\), Herslund et al.\(^{22}\);
(\(\bigcirc\) ) CP/CO\(_2\), Herslund et al.\(^{22}\) .................................................................................. 25
Figure 2.16 \(\text{CO}_2\) H-L-W equilibrium curves for pure water, 500 ppm SDS and 5mol\% THF
and induction point for THF 5 mol\%, SDS- 500ppm and SDS-500ppm/THF-5mol%.
Sources: no additive; SDS-500ppm, THF 5 mol\%, THF- induction, SDS-induction
and SDS/THF induction\(^{124}\) ........................................................................................................... 26
Figure 2.17 CO₂+THF+H₂O system. For clarity reasons, the systems are presented by two numbers in brackets. The first number denotes the mol fraction of CO₂ of a potential binary gas mixture and the second one denotes the promoter concentration. References are presented according to their presence in figure from left to right............................................................27

Figure 2.18 CO₂+CH₄+TBAB+H₂O system. For clarity reasons, the systems are presented by two numbers in brackets. The first number denotes the mol fraction of CO₂ in CO₂+CH₄ gas mixture and the second one denotes the promoter concentration. References are presented according to their presence in figure from left to right..............28

Figure 2.19 CO₂+H₂+TBAB+H₂O system. For clarity reasons, the systems are presented by two numbers in brackets. The first number denotes the mol fraction of CO₂ in CO₂+H₂ gas mixture and the second one denotes the promoter concentration. References are presented according to their presence in figure from left to right.................................................................30

Figure 2.20 CO₂+TBAB+H₂O systems. For clarity reasons, the systems are presented by two numbers in brackets. The first number denotes the mol fraction of CO₂ of a potential binary gas mixture and the second one denotes the promoter concentration. References are presented according to their presence in figure from left to right.................................................................31

Figure 2.21 CO₂+TBAC+H₂O systems. For clarity reasons, the systems are presented by two numbers in brackets. The first number denotes the mol fraction of CO₂ of a potential binary gas mixture and the second one denotes the promoter concentration. References are presented according to their presence in figure from left to right.................................................................32

Figure 2.22 CO₂+TBAF+H₂O systems. For clarity reasons, the systems are presented by two numbers in brackets. The first number denotes the mol fraction of CO₂ in CO₂+N₂ gas mixture and the second one denotes the promoter concentration. References are presented according to their presence in figure from left to right.................................................................32

Figure 2.23 CO₂ + CP + H₂O system ................................................................................33

Figure 2.24 CO₂ + CH₄ + THF + H₂O system...................................................................33

Figure 3.1 Absolute uncertainty of pressure transducer for 0-10 bar ................................35

Figure 3.2 Absolute uncertainty of pressure transducer for 0-100 bar.............................36

Figure 3.3 Absolute uncertainty of temperature transducer .............................................36

Figure 3.4 CO₂ volume error against peak area as measured with GC..............................37

Figure 3.5 N₂ volume error against peak area as measured with GC..............................38

Figure 3.6 Simplified schematic diagram of equilibrium cell equipment. LNP: liquid nitrogen container. VP: vacuum pump. SD:stirring device. TR: temperature regulator. TT: temperature transducer bottom. PT: pressure transducer top. PC: personal computer...39

Figure 3.7 Cylinder of CO₂ and N₂ gas mixture..............................................................40

Figure 3.8 The water bath in which the equilibrium cell is immersed with the transducers attached to it.................................................................40

Figure 3.9 The inner volume of the equilibrium cell is approximately 125ml.....................41

Figure 3.10 Temperature trace method for determination of equilibrium point of CO₂/N₂ (6.87/93.13) gas mixture with 20 wt% TBAB mol fraction.........................................................44
Figure 3.11  Hydrate dissociation points for different systems using TBAB as promoter. The Figure contains systems of this work and systems of CO₂+N₂+TBAB+H₂O from literature. For clarity reasons, the systems are presented by two numbers in brackets. The first number denotes the mol fraction of CO₂ in CO₂+N₂ gas mixture cylinder and the second one denotes the promoter concentration. Black markers connected with trendlines correspond to results of this work. References are presented according to their presence in figure from left to right.

Figure 3.12  Hydrate dissociation points for different systems using TBAB as promoter. The Figure contains systems of this work and systems of CO₂+TBAB+H₂O from literature. For clarity reasons, the systems are presented by two numbers in brackets. The first number denotes the mol fraction of CO₂ in CO₂+N₂ gas mixture cylinder and the second one denotes the promoter concentration. Black markers connected with trendlines correspond to results of this work. References are presented according to their presence in figure from left to right.

Figure 3.13  Hydrate equilibrium points for different systems using TBAB as promoter. The Figure contains systems of this work and systems of N₂+TBAB+H₂O from literature. For clarity reasons, the systems are presented by two numbers in brackets. The first number denotes the mol fraction of CO₂ in CO₂+N₂ gas mixture cylinder and the second one denotes the promoter concentration. Black markers connected with trendlines correspond to results of this work. References are presented according to their presence in figure from left to right.

Figure 3.14  Hydrate equilibrium points for different systems using CP promoter. References are presented according to their presence in figure from left to right. For clarity reasons, the systems are presented by two numbers in brackets. The first number denotes the mol fraction of CO₂ in CO₂+N₂ gas mixture cylinder and the second one denotes the promoter concentration. Black markers connected with trendlines correspond to results of this work. References are presented according to diagram from left to right.

Figure 3.15  Hydrate dissociation points for different systems using TBAF as promoter with CO₂ + N₂ (0.48/99.52) gas mixture. References are presented according to diagram from left to right. The first number denotes the mol fraction of CO₂ in CO₂+N₂ gas mixture cylinder and the second one denotes the promoter concentration used in this work. Black markers connected with trendlines correspond to results of this work. References are presented according to diagram from left to right.

Figure 3.16  Hydrate equilibrium points for different systems using TBAB promoter and mixture of TBAB+CP in this study. References are presented according to diagram from left to right. The first number denotes the mol fraction of CO₂ in CO₂+N₂ gas mixture cylinder, the second one denotes the promoter concentration and the third number is the 5 vol% of CP used in this work. Black markers connected with trendlines correspond to results of this work. References are presented according to their presence in figure from left to right.

Figure 3.17  Hydrate dissociation points for different systems using TBAF and CP as promoter with CO₂ + N₂ (0.48/99.52) gas mixture. The first number denotes the mol fraction of CO₂ in CO₂+N₂ gas mixture cylinder, the second one denotes the promoter concentration and the third number is the 5 vol% of CP used in this work. Black markers connected with trendlines correspond to results of this work. References are presented according to their presence in figure from left to right.
Figure 3.18 Temperature and pressure hydrate equilibrium points for CO₂+N₂+TBAF/TBAB/CP+H₂O system. The first number denotes the mol fraction of CO₂ in CO₂+N₂ gas mixture cylinder, the second one denotes the promoter concentration and the third number is the 5 vol% of CP used in this work. The open blue colors, red and green are TBAB results. The purple denote CP results and the dark blue stand for TBAF results. All results of this work are connected with trendlines. References are presented according to diagram from left to right ................................................................................................... 56

Figure 4.1 Pressure-Temperature trace method diagram for estimating hydrate dissociation point. In this case for 20 wt% TBAB and CO₂/N₂ (6.87/93.13) the dissociation point is found at 32.85 bar and 12.94 °C ....................................................... 59

Figure 5.1 Algorithm used for incipient hydrate dissociation pressure calculations for a hydrate forming system of specified composition and temperature 20. Only for qCPA calculations, the code was developed such that initial pressure estimation is not needed ...................................................................................................... 83

Figure 5.2 Hydrate dissociation points for different systems using CP as promoter and the predictive curves of vdw-P model coupled with CPA EoS for fluid phases. For clarity reasons, the systems are presented by two numbers in brackets. The first number denotes the mol fraction of CO₂ in N₂ gas mixture cylinder and the second one denotes the promoter concentration. Black markers connected with trendlines correspond to results of this work. References are presented according to their presence in figure from left to right. The upper line is produced based on feed composition data from this work. The bottom line is produced based on an assumed feed composition ................... 89

Figure 5.3 Hydrate phase equilibria points and the predictive curve of the system CO₂+CC₇+H₂O 194 .............................................................................................................. 90

Figure 5.4 Hydrate phase equilibria points and the predictive curve of the system CO₂+CC₈+H₂O 194 .............................................................................................................. 90

Figure 5.5 Hydrate phase equilibria points and the predictive curve of the system CO₂+CC₆+H₂O 72 ............................................................................................................... 90

Figure 5.6 Hydrate phase equilibria points and the predictive curve of the system of CO₂+mCP+H₂O 72 .......................................................................................................... 91

Figure 5.7 Hydrate phase equilibria and the predictive curve of the system of CO₂+mCC₆+H₂O 72 .............................................................................................................. 91

Figure 5.8 Hydrate phase equilibria points and the predictive curves for CPA and qCPA EoS of the ternary system CO₂+CP+H₂O 72,133. Only for the qCPA case, the model is implemented in MATLAB by Martin Gamel Bjørner .......................................................... 91

Figure 6.1 CO₂ avoidance costs and avoidance rates for iron and steel production in the short-mid term future (10-15 years) and the long term future (20 years or more). The error bars present uncertainty ranges. The dotted lines indicate the probable future CO₂ price range (30-75 Euro/t) 10 ......................................................................................................................... 98

Figure 6.2 CO₂ gas uptake for every gas hydrate structure 196 .......................................................................................................................... 99

Figure 6.3 Normalised rate of hydrate growth and gas uptake against various promoters for different reactor configurations 196 ................................................................................ 100

Figure 6.4 A hybrid hydrate-membrane process for CO₂ recovery from flue gas 7 ..................................................................................................................... 101
# Table of Contents

1. Introduction .......................................................................................................................... 1  
   1.1 CO₂ capture via gas hydrate crystallization ................................................................. 2  
       1.1.1 Gas hydrate promotion .................................................................................. 2  
   1.2 Scope of the project ..................................................................................................... 4  
   1.3 Thesis structure ......................................................................................................... 4  

2. Theory on hydrate promotion .............................................................................................. 6  
   2.1 Hydrate Structures ......................................................................................................... 7  
       2.1.1 The “Memory Effect” Phenomenon ................................................................. 10  
       2.1.2 Phase diagram .............................................................................................. 11  
   2.2 Gas hydrates usage ...................................................................................................... 12  
       2.2.1 Energy supply from gas hydrate reservoirs .................................................. 12  
       2.2.2. Hydrates for gas storage .............................................................................. 12  
       2.2.3 Gas hydrates applications in separation processes ........................................ 13  
   2.3 Hydrate measurements ................................................................................................. 14  
       2.3.1 Hydrate dissociation methods ........................................................................ 14  
       2.3.2 Macroscopic and microscopic techniques ..................................................... 16  
   2.4 Thermodynamic promoters ......................................................................................... 19  
       2.4.1 Hydrate promotion ......................................................................................... 19  
       2.4.2 Critically Reviewed PT diagrams for CO₂ + promoter systems + H₂O ......... 26  
   2.5 Conclusions ............................................................................................................... 33  

3. Experimental methodology ............................................................................................... 34
# Table of Contents

3.1 Equipment used ........................................................................................................... 35  
  3.1.1 Calibration of pressure and temperature transducers ........................................ 35  
  3.1.2 Calibration of Gas Chromatograph ..................................................................... 37  
3.2 Hydrate equipment description ...................................................................................... 38  
  3.2.1 Measuring procedure ........................................................................................... 41  
3.3 Hydrate equilibrium results ........................................................................................ 44  
  3.3.1 TBAB results ........................................................................................................ 44  
  3.3.2 Results for CP as promoter ................................................................................. 48  
  3.3.3 TBAF results ........................................................................................................ 50  
  3.3.4 Mixtures of TBAB+CP and TBAF+CP ................................................................. 52  
3.4 Conclusions .............................................................................................................. 55  

4 Experimental uncertainties and consistency analysis of results ................................ 58  
  4.1 Calculation of hydrate equilibrium point ................................................................. 59  
  4.2 Hydrate equipment and random uncertainties ........................................................... 60  
  4.3 Gas mixture uncertainties ......................................................................................... 61  
  4.4 Molar composition uncertainties .............................................................................. 63  
  4.5 Consistency analysis of hydrate equilibrium data ......................................................... 64  
  4.6 Conclusions .............................................................................................................. 67  

5 Thermodynamic modeling ............................................................................................ 69  
  5.1 Introduction .............................................................................................................. 70  
  5.1.1 Summary of modeling results in literature ........................................................... 70  
  5.1.2 Paricaud’s model .................................................................................................. 71  
  5.2 The van der Waals-Platteeuw Hydrate Model .............................................................. 72  
  5.3 Cubic-Plus-Association (CPA) .................................................................................. 78  
  5.4 Algorithm Applied to this work ................................................................................. 81  
  5.5 Model Parameters ..................................................................................................... 84  
  5.5.1 Hydrate Model .................................................................................................... 84  
  5.5.2 Equation of State (CPA) ..................................................................................... 86  
  5.6 Modeling Results ..................................................................................................... 88  
  5.7 Conclusions – Looking ahead on modeling of TBA salts ............................................ 92  

6 Conclusions – Future work .......................................................................................... 94
# Table of Contents

6.1 Conclusions .......................................................................................................................... 95
6.2 Future steps to technological scale-up ................................................................................ 97
   6.2.1 Process design aspects ............................................................................................... 97
   6.2.2 Future work ................................................................................................................. 101

**Bibliography** .......................................................................................................................... 103

Appendix A ................................................................................................................................ 119
Appendix B ................................................................................................................................ 129
Appendix C ................................................................................................................................ 133
Appendix D ................................................................................................................................ 140
Appendix E ................................................................................................................................ 144
Mεγίστη πρᾶξις ἐστιν ἡ ἀπραξία.

Άγ. Γρηγόριος ὁ Θεολόγος (329 – 390 μ.Χ.)

=Greatest action is inaction.

St. Gregory the Theologian (329 – 390 AD)
1.1 CO₂ capture via gas hydrate crystallization

Climate change is and will become further an issue of major international concern. The most significant geopolitical consequences include human migrations due to starvation, which is apparent many years now in sub-Saharan Africa. It has been very vividly shown in the late decades that carbon dioxide is an important contributor to climate change\(^1\)\(^2\). In this context, the technology of carbon capture and storage (CCS) has received increasing heed over the last decades as a potential method of limiting atmospheric emissions of carbon dioxide (CO₂)\(^3\)\(^4\) from flue gas of power and process plants.

Carbon capture techniques are categorized based on which point of the process CO₂ is captured. In that sense, the approaches are post-combustion capture from power plant flue gases using amine-based solvents such as Monoethanolamine (MEA) and ammonia; pre-combustion capture (also via chemical solvents) from the synthesis gas produced in an integrated coal gasification combined cycle (IGCC) power plant; and oxy-combustion capture, in which high-purity oxygen gas rather than air is utilized for combustion in a pulverized coal (PC) power plant to produce a flue gas with a high CO₂ concentration of which is suitable for capture without a post-combustion chemical process\(^5\). The approaches are shown in Figure 1.1.

In a pulverized power plant, which emits low CO₂ emissions, various types of techniques are currently under investigation. They are differentiated based on liquid solvents (e.g. Monoethanolamine (MEA)) or dry regenerable solvents (e.g. activated coal, Na-, K-, Ca-carbonates) and membrane separation. Membrane material can be zeolites, polymers, silica, ceramic or enzyme-based. In addition, metal organic frameworks (MOF) can be used either as sorbents or membranes. They are constituted by a metal ion (Mg, Zn) and an organic ligand. Finally, cryogenic separation or hydrate crystallization is possible solutions. In cryogenic separation, the refrigerants used are CH₄, C₂H₆, C₃H₈, C₄H₁₀ and mixtures of them\(^5\).

Gas hydrate crystallization is to be used as a post-combustion capture process\(^6\)\(^-\)\(^8\) in oil and gas industry. The scope of this method is to capture CO₂ from flue gas by means of hydrates and then the release of CO₂ so that CO₂ is purely concentrated in one stream.
This technology is still immature and requires high pressure for the hydrates to form. High pressure is linked with high operational costs\textsuperscript{9,10}. Therefore, organic and inorganic chemicals (promoters) are tested recently which reduce the hydrate formation pressure\textsuperscript{11-15}. The chemicals used in this study are tetra-n-butyl ammonium salts and cyclopentane. The experimental results were produced in MINESParisTech in Fontainebleau (March – October 2014).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{carbon_capture_methods.png}
\caption{Carbon capture methods\textsuperscript{16}.}
\end{figure}

\subsection{1.1.1 Gas hydrate promotion}

Promoters are chemicals that shift the hydrate equilibrium line to higher temperatures and lower pressures. In this study, the focus was on tetrabutyl derivatives of ammonium salts and on an organic and hydrophobic compound; cyclopentane (CP).

In general, the polyhydrates of peralkylammonium salts, which are included in ionic clathrate hydrates according to G. Jeffrey’s classification\textsuperscript{17}, are inclusion compounds that exhibit both hydrophilic and hydrophobic hydration. Depending on the charge, an anion replaces one or several water molecules in the water host lattice to form hydrogen bonds (hydrophilic hydration). A cation is also incorporated into cavities of the water-anion framework displacing water molecule with nitrogen atom, so that distances between the
cation atoms and water framework atoms are no less than a sum of their van der Waals radii (hydrophobic hydration). An interesting feature of these compounds is that within a narrow range of concentrations, the same salt may form several ionic clathrate hydrates with different structures, albeit with similar stoichiometry and thermal stability. Cyclopentane forms in general s(II) structure which is one the three main hydrate structures.

1.2 Scope of the project
The purpose of this project is to develop a solid experimental and theoretical framework for better comprehending and addressing the problems of CO$_2$ hydrates in oil and gas industry and for enhancing the utilization of hydrate crystallization as a CO$_2$ capture technology. To achieve this goal, new experimental data were produced targeting on pressure-temperature (PT) measurements which can reveal profoundly the impact and usefulness of various potential hydrate promoters. To familiarize oneself with this topic, a proper model for the experimental data has been used based on van der Waals and Platteeuw hydrate model. The model was previously developed in CERE, DTU and successfully used in modeling gas hydrate data. This model describes only the solid hydrate phase and is typically combined with Cubic-Plus-Association equation of state (CPA EoS) and an activity coefficient model for the description of co-existing fluid phases. The solid phase is treated as a solid solution of hydrate formers in a crystalline host lattice.

1.3 Thesis structure
The chapters of this thesis are described below.

Chapter 2: Theory on hydrate promotion
- Hydrate theory
- Hydrate measuring techniques
- Critically Reviewed PT diagrams for CO$_2$+promoter systems

Chapter 3: Experimental methodology
Chapter 1: Introduction

- Calibration of instruments
- Measuring procedure
- Hydrate equilibrium results

Chapter 4: Experimental uncertainties and consistency analysis of results

- Hydrate equipment and random uncertainties
- Molar composition uncertainties
- Consistency analysis of results

Chapter 5: Thermodynamic modeling

- The van der Waals-Platteeuw Hydrate Model
- Cubic-Plus-Association (CPA)
- Modeling Results

Chapter 6: Conclusions – Future work

- Conclusions, process design aspects and future work
When the soul ascends in her theory above and spreads out her meanings in (what exist in) heaven and lures those that by the eyes of body cannot be seen, and flesh doesn’t rule them, then faith constitutes everything.

Abbas Isaac the Syrian (630 – 699 AD)
2.1 Hydrate Structures

Natural gas hydrates are crystalline solids composed of water and gas. The gas molecules (guests) are captured in water cavities (host) that consists of hydrogen-bonded water molecules. Gas molecules which typically form hydrates are methane, ethane, propane and carbon dioxide. The research efforts on natural gas hydrates can be categorized into three historical phases:

- The first period covers from their discovery (1810) until today and is interested on gas hydrates chemistry and research.
- The second period, continuing from 1934 until the present, predominantly refers to man-made gas hydrates as a hitch to the natural gas industry.
- The third period, from the mid-1960s until the present, enlightens hydrate aspect as a potential energy source, in situ in both the deep oceans and permafrost regions as well as in extraterrestrial environments.

In present, the concern on hydrates is growing more the last years due to environmental concerns. The growth in hydrate-related articles follows historically exponential growth from the 1930s and in general the research on hydrates started in early 1800s.

All common natural gas hydrates belong to the three crystal structures, cubic structure I s(I), cubic structure II s(II), or hexagonal structure H s(H) shown in Figure 2.1. The major contrast to ice is that ice forms as a pure component, while hydrates will not form without guests of the proper size.

The structure s(I) is formed with guest molecules of which diameters are among 4.2Å and 6Å, such as methane, ethane, carbon dioxide, and hydrogen sulfide. N₂ and small molecules including H₂ (for d<4.2Å) form s(II) as single guests. Larger single guest molecules (6Å<d<7Å) such as propane or iso-butane will form s(II). For molecules typically 7Å<d<9Å such as iso-pentane, neo-hexane (2, 2-dimethylbutane) or cyclooctane can form s(H) when accompanied by smaller molecules such as CH₄, H₂S, or N₂.
In CO₂+N₂ gas mixture, carbon dioxide is only captured in large cages of s(I) structure. Methane is captured either in small or large cavities of s(I) structure due to their small size. The Table 2.1 shows these common structures.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Cavity type</th>
<th>Guest molecule diameter (Å)</th>
<th>No. of cavities in unit cell (small/medium/large)</th>
<th>No. of H₂O molecules in cavity (small/medium/large)</th>
</tr>
</thead>
<tbody>
<tr>
<td>s(I)</td>
<td>$5^{12}$</td>
<td>$5^{12}6^2$</td>
<td>4.2 – 6</td>
<td>2/-/6</td>
</tr>
<tr>
<td>s(II)</td>
<td>$5^{12}$</td>
<td>$5^{12}6^4$</td>
<td>6 – 7 or &lt; 4.2</td>
<td>16/-/8</td>
</tr>
<tr>
<td>s(H)</td>
<td>$5^{12}$</td>
<td>$4^{15}6^3$</td>
<td>$5^{12}6^8$</td>
<td>3/2/1</td>
</tr>
</tbody>
</table>

The next Figure 2.1 shows the diversity of the most common cavities.

![Figure 2.1](image)

**Figure 2.1** Gas Hydrate main structures: (a) pentagonal dodecahedron ($5^{12}$), (b) tetrakaidecahedron ($5^{12}6^2$), (c) hexakaidecahedron ($5^{12}6^4$), (d) irregular dodecahedron ($4^{15}6^3$) and (e) icosahedron ($5^{12}6^8$).

The $5^{12}$ cavity in a gas clathrate hydrate denotes pentagonal dodecahedron (12-sided cavity) because it has 12 pentagonal faces with equal edge lengths and, thus, equal angles. Similarly, the $5^{12}6^2$ cavity represents tetrakaidecahedron (14-sided cavity).
because of the 12 pentagonal and 2 hexagonal faces. The hexakaidecahedral cavity (16-hedron) is denoted $5^{12}6^4$ due to the 12 pentagonal faces and the 4 hexagonal faces. The irregular dodecahedron cavity ($4^35^66^3$) has 3 square faces, 6 pentagonal faces and 3 hexagonal faces. The largest icosahedron cavity ($5^{12}6^8$) has 12 pentagonal faces and 6 hexagonal faces and a hexagonal face each at the cavity crown and foot$^{24}$.

Less common clathrate hydrates exist that are formed by compounds other than natural gas guests (such as Jeffrey’s structures III–VII, structure T, complex layer structures) and high pressure hydrate phases. Clathrate hydrate crystals are composed of cage structures formed by water molecules, and each of these cages can encapsulate a gas molecule. The structures consist of several types of cages, depending on the encaged gas molecules$^{24}$. Clathrate hydrates encaging gas molecules (gas hydrates) are stable only under high pressure and low temperature. An exception is tetra-n-butylammonium bromide (TBAB) which forms a semiclanthrate hydrate crystal with water molecules even at atmospheric pressure. Such a hydrate is called a semi-clathrate hydrate crystal because a part of the cage structure is broken in order to encapsulate the large tetra-n-butylammonium molecule. In TBAB semi-clathrate hydrate, the $\text{Br}^-$ anion forms cage structures with water and the tetra-n-butylammonium cation occupies four cages$^{27}$ as shown in Figure 2.2.
2.1.1 The “Memory Effect” Phenomenon

There has been a consensus among hydrate researchers that hydrates retain a “memory” of their structure when melted at moderate temperatures. Consequently, hydrate forms more easily from gas and water obtained by melting hydrate, than from fresh water with no previous hydrate history. Conversely, if the hydrate system is heated sufficiently above the hydrate formation temperature at a given pressure, the “memory effect” disappears. The time for a hydrate cell to appear in the aqueous solution is called induction time. In Table 2.2, observations of this phenomenon are denoted.

<table>
<thead>
<tr>
<th>Observations</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrates form more readily from melted hydrate</td>
<td>Makogon\textsuperscript{29}</td>
</tr>
<tr>
<td>Thermal history of water affects hydrate induction times,</td>
<td>Vysniauskas and Bishnoi\textsuperscript{30}</td>
</tr>
<tr>
<td>that is, time of hot/warm water higher than thawed ice or hydrate</td>
<td>Lederhos\textsuperscript{31}, Parent and</td>
</tr>
<tr>
<td></td>
<td>Bishnoi\textsuperscript{32}, Takeya et al.\textsuperscript{33},</td>
</tr>
<tr>
<td></td>
<td>Ohmura et al.\textsuperscript{34}</td>
</tr>
<tr>
<td>Successive cooling curves show decreased metastability from the vapor–liquid–hydrate line</td>
<td>Schroeter et al.\textsuperscript{35}</td>
</tr>
<tr>
<td>Induction period is eliminated by re-forming hydrate on an ice surface preexposed to xenon</td>
<td>Moudrakovski et al.\textsuperscript{36}</td>
</tr>
<tr>
<td>Induction times decrease when hydrate is reformed from hydrate decomposed for 1 h compared to 12 h</td>
<td>Lee et al.\textsuperscript{37}</td>
</tr>
<tr>
<td>Hydrate morphology depends on the dissociation conditions before reformation. A rough surface forms from hydrates decomposed for $\geq 24$ h, while a smooth surface forms from hydrates decomposed for only 30 min</td>
<td>Servio and Englezos\textsuperscript{38}</td>
</tr>
</tbody>
</table>
2.1.2 Phase diagram

A general axiom in thermodynamics is called Gibbs phase rule. The phase rule is shown in Eq. 2.1:

\[ F = 2 + C - Z \]  (2.1)

where \( F \) are the degrees of freedom, \( C \) are the number of components, and \( Z \) are the number of phases in thermodynamic equilibrium between each other. For example, a single component existing as a vapor and a liquid has one degree of freedom. If the pressure is specified, then there are zero degrees of freedom—the temperature is fixed.

In gas hydrates, two components are at least present (binary systems). From Eq. 2.1, if \( N = 2 \) and for two phases e.g. a system of water and a gas, the degree of freedom, \( F \), becomes equal to two and, thus, the hydrate area can be presented in a 2-D diagram of \( P, T \) as shown in Figure 2.3.

![Figure 2.3](image)

The intersection of four three-phase loci is called quadruple point. There are two quadruple points \((Q_1, Q_2)\) which are denoted by the equilibrium phases. The hydrate
region is bounded by three lines: I–H–V at conditions below Q1, line LW–H–V between Q1 and Q2, and line LW–H–LHC at conditions higher than Q2. An upper quadruple point, Q2, is often considered as the maximum temperature of hydrate formation because line LW–H–LHC is almost vertical. Note that N₂ and CH₄ do not have Q₂. This is because N₂ and CH₄ have critical temperatures at 191 and 126 K respectively, which are far lower to the quadruple point Q₁ and, thus, the intersection of the vapor pressure line with the LW–H–V line above 273 K is occluded²⁴.

The experimental results of this work include a quaternary system of three phases, so the available degrees of freedom are three which are the gas composition, aqueous solution composition and the pressure. If these are fixed, an invariant hydrate equilibrium point is obtained for every different temperature value. In that sense, by changing pressure of the system, a new temperature equilibrium point is attained.

2.2 Gas hydrates usage
   2.2.1 Energy supply from gas hydrate reservoirs
Gas hydrates reserves in the earth can be implemented as a (natural) gas supply to cover the increasing energy gap of the world economy. The estimated amount of in situ gas reserves is approximately 10¹⁶ m³ for methane hydrate³⁹. In addition, several estimations show that there are worldwide more organic carbon reserves as methane hydrates than all other forms of fossil fuels⁴⁰. It is currently believed that if only 1% of the estimated methane hydrate reserves are recovered, it will be sufficient for the US to satisfy its energy demands for the next eight decades⁴¹. Although there is no commercial scale plant for exploiting gas hydrate reserves, it is still regarded as a promising approach of which harvest should begin in the next 15 years, mainly due to the rapid depletion of conventional natural gas reservoirs⁴².

2.2.2. Hydrates for gas storage
Several studies indicate that the gas hydrate structures can become potential storage media for various gases³,⁴³,⁴⁴. Gas hydrate technology for storage and transportation has the advantage of safety for the given processes, as well as much lower process volumes compared to conventional storage methods like liquefaction. Detailed economic studies
show that the capital cost for natural gas transportation with hydrate technology is 48% lower than that for the conventional liquefied natural gas (LNG) technique, mainly due to lower investment in infrastructure and equipment\textsuperscript{45}. However, LNG-type gas transportation is currently preferred for distant markets or transportation of natural gases produced from huge gas fields because of expensive capital investment\textsuperscript{45}. On the contrary, there are reports proposing that gas hydrates are economically more cost effective for storage and transportation of standard gas (gas streams of small quantity, especially those far from the pipeline) compared to the LNG method\textsuperscript{46-48}.

### 2.2.3 Gas hydrates applications in separation processes

The capture of CO\textsubscript{2} and sequestration (CCS) has become an important area of research for treating CO\textsubscript{2} emissions\textsuperscript{49}. CO\textsubscript{2} separation is the most expensive step of the CCS process\textsuperscript{50,51}. The effort is to develop energy efficient and environmental friendly technologies to capture the CO\textsubscript{2} produced in large scale power-plants, where mostly CO\textsubscript{2} and N\textsubscript{2} in the flue gas is typically contained\textsuperscript{52}. One novel approach to separate CO\textsubscript{2} from combustion flue gas is via gas hydrate crystallization techniques\textsuperscript{50-52}. When hydrate crystals are formed from a binary mixture of these gases, the different attraction between CO\textsubscript{2} and other gases in the hydrate cages will enrich the hydrate phase in CO\textsubscript{2} and the gas phase in other gases. The hydrate phase is then dissociated by depressurization and/or heating and thus CO\textsubscript{2} is retrieved\textsuperscript{52}. According to experimental results\textsuperscript{9}, CO\textsubscript{2} selectivity in the hydrate phase is at least four times higher than that in the gas phase. For efficient design of such processes, reliable phase equilibrium data are required.

Methane (CH\textsubscript{4}) is a gas with 21 times greater impact on global warming than that of CO\textsubscript{2} and it contributes to 18% of the total global greenhouse effects\textsuperscript{53}. This component is the major constituent of natural gas and its reserves in the form of hydrates in the earth. Therefore, methane separation from emitted industrial gas streams has heeded significant attention in the last few decades. Recently, novel separation processes using gas hydrate formation phenomena have been proposed in the literature\textsuperscript{45,47-49}. Economic studies for such processes would focus mainly on the price of the promoters needed to reduce the pressure and increase the temperature of the separation steps.
because the design of other required equipment is generally simple. It seems that the industry will be interested in such investments whenever the environmental regulations are rigid and when the natural gas reserves tend to reach their half-lives. Gas hydrate can also be used to remove acid gases during gas processing. When reservoir content high quantities of acid gases (CO₂, H₂S), a pre-treatment can be to reduce the concentration of acid gases by using gas hydrates while the pressure is very high. Then the concentration of acid gases is reduced before utilization of amines. Other uses of hydrates include the field of oil and gas separation, desalination process, food engineering, biotechnology and separation of ionic liquids.

### 2.3 Hydrate measurements

#### 2.3.1 Hydrate dissociation methods

The hydrate dissociation is a reversible process which can be defined as the point of temperature and pressure where the last hydrate crystal melts. There are experimental procedures for measuring hydrate dissociation conditions as in Table 2.3 are shown.

<table>
<thead>
<tr>
<th>Method</th>
<th>Experimental procedure</th>
<th>Hydrate formation</th>
<th>Hydrate dissociation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isothermal</td>
<td>Constant temperature</td>
<td>Temperature increase</td>
<td>Visual observation of hydrate crystal disappearance</td>
</tr>
<tr>
<td>Isobaric</td>
<td>Constant pressure</td>
<td>Exchange of gas or liquid from an external reservoir</td>
<td>Intersection point of cooling and heating isochors (nonvisual technique)</td>
</tr>
<tr>
<td>Isochoric</td>
<td>Constant volume</td>
<td>Pressure decrease</td>
<td></td>
</tr>
</tbody>
</table>

In the isothermal and isobaric methods, where the pressure and temperature are held constant respectively, the equilibrium conditions are determined by visual observation of phase change: hydrate crystals disappearance. The most widely used method is the isochoric one.

In a typical isochoric experiment, by decreasing the system’s temperature, hydrates start forming. The differential pressure change ($\partial P$) with respect to differential temperature
change ($\partial T$) is measured in a constant volume cell. At every load of known composition, pressure is monitored as a function of temperature so that PT isochor will be produced. The quantity ($\partial P/\partial T)_V$ indicates the slope of an isochoric line in a PT phase diagram. In the end, hydrates dissociation occurs through stepwise heating. The intersection of cooling and heating curves depicts a phase transition and the hydrate dissociation ($P,T$) point is revealed. For a given load, by plotting several experimental isochors produced at different pressures, the complete hydrate phase boundary of a system is created.

In the isochoric method, the equilibrium condition is recognized through temperature and pressure measurement. This method includes no visual observation or complicated calculations so reliable hydrate equilibrium data are obtained. In addition, the technique covers the entire range of hydrate formation temperatures and pressures and, thus, fewer amounts of fluids are implemented due to the elimination of volume changes. Moreover, the technique is aligned to automated control of experiments. Thus, isochoric method, compared to isobaric and isothermal, is regarded more convenient for investigating phase behavior of multicomponent mixtures. The $P,T$ path for determination of hydrate equilibrium point is shown in Figure 2.4.

More specifically, researchers used CO$_2$-H$_2$ (40:60) mixture gas hydrate systems with TBAB additives to investigate the kinetic characteristics under the same driving force condition. The volume is kept constant and the temperature was changed during the experiment. The procedure is as follows: as the cell temperature was lowered, the pressure decreased linearly without hydrate formation occurring (from point A to B) due to the gas contraction as well as increased gas solubility upon cooling at constant volume. At point B, the hydrates started to form and the pressure dropped rapidly to point C. The catastrophic growth was observed from point B to C. Hydrate dissociation began when the cell was heated from point C but hydrate was remaining until Point D. Between points C and x, the cell temperature was rapidly increased, and waited at least 5 h until reaching equilibrium condition. To avoid obtaining an erroneous dissociation temperature and pressure, the dissociation part of the loop must be performed at a heating rate sufficiently slow to allow the system to reach equilibrium: heating rate of about 0.1 K/h from point x
to D. Finally, the hydrate equilibrium condition (or hydrate dissociation temperature and pressure) is determined at point D.\(^{58}\)

![Figure 2.4](image.png)

**Figure 2.4** Temperature and pressure trace for determination of equilibrium point of CO\(_2\)-H\(_2\) (40:60) mixture gas hydrate systems with TBAB additives at initial temperature of 293.15 K and pressure of 0.99 MPa.\(^{57}\)

### 2.3.2 Macroscopic and microscopic techniques

For macroscopic hydrate experiments, the most common techniques used are:\(^{24}\): High pressure visual autoclave cell, Figure 2.5, rocking cell, Figure 2.6, Quartz Crystal Microbalance (QCM) in high pressure cell, Figure 2.7, and High-pressure Differential Scanning Calorimetry (HP-DSC), Figure 2.8.

High pressure visual autoclave cell can determine \(P_{\text{diss}}, T_{\text{diss}}\), gas consumption rate during growth/decomposition and visual imaging of growth/decomposition. Quartz Crystal Microbalance (QCM) is also used for \(P_{\text{diss}}, T_{\text{diss}}\). Its major advantage is the small samples (in the order of mg) so equilibration times (hence experimental time) reduced.\(^{24}\) According to Lee *et al.*\(^{59}\), the experimental time can be reduced nearly 30 times. Rocking cell is
typically used for Low Dosage Hydrate Inhibitor (LDHI) testing and can specify $P_{\text{diss}}, T_{\text{diss}}$ and gas consumption rate during growth/decomposition.

Finally, High-pressure Differential Scanning Calorimetry (HP-DSC) can delimitate $T_{\text{diss}}$, heat capacities, heat of dissociation, gas hydrate structure, emulsion stability and hydrate agglomeration. The Table 2.4 summarizes the techniques.

**Table 2.4** Most common techniques for macroscopic hydrate measuring$^{24}$. 

![Figure 2.5 Schematic diagram of high pressure visual autoclave cell$^{60}$.](image1)

![Figure 2.6 Rocking cell apparatus$^{24}$.](image2)

![Figure 2.7 Quartz crystal microbalance apparatus$^{59}$.](image3)

![Figure 2.8 DSC device: R, reference vessel; M, sample vessel$^{61}$.](image4)
Chapter 2  
Theory on hydrate promotion

<table>
<thead>
<tr>
<th>Technique</th>
<th>Phase equilibria data</th>
<th>Kinetic data</th>
<th>Other info</th>
</tr>
</thead>
<tbody>
<tr>
<td>High pressure visual autoclave cell</td>
<td>( P, T )</td>
<td>( P(t), T(t) ), film growth rate vs time</td>
<td>Sapphire/quartz window limits: typically 35 MPa Stirred</td>
</tr>
<tr>
<td>Quartz Crystal Microbalance (QCM)</td>
<td>( P, T )</td>
<td>( P(t), T(t) )</td>
<td>Typically 40 MPa</td>
</tr>
<tr>
<td>Rocking cell (isochoric technique)</td>
<td>( P, T )</td>
<td>( P(t), T(t) )</td>
<td>Typically 70 MPa (blind cell); 35 MPa (visual cell) Stirred</td>
</tr>
<tr>
<td>High-pressure differential scanning calorimetry</td>
<td>( P, T )</td>
<td>Hydrate phase vs. time</td>
<td>&lt;40 MPa, 230 – 400 K</td>
</tr>
</tbody>
</table>

New apparatuses have been also recently proposed\(^{62,63}\).

**Table 2.5** Most common techniques for microscopic hydrate measuring\(^{64}\).

<table>
<thead>
<tr>
<th>Technique</th>
<th>Phase equilibria data</th>
<th>Kinetic data</th>
<th>Other info</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid-state NMR spectroscopy</td>
<td>Hydrate phase and structure</td>
<td>Hydrate phase vs time (min)</td>
<td>typically 0.1 MPa, or use glass bulbs &lt;7 MPa</td>
</tr>
<tr>
<td>Raman spectroscopy with high pressure windowed cell</td>
<td>Hydrate phase and structure</td>
<td>( P(t), T(t) ), hydrate phase vs time (min)</td>
<td>typically for sapphire window &lt;70 MPa (for capillary tubes &lt;420 MPa; diamond anvil cell GPa’s)</td>
</tr>
<tr>
<td>X-ray diffraction (lab/synchrotron)</td>
<td>Hydrate, water and gas phase distribution and structure</td>
<td>( P(t), T(t) ), hydrate phase vs time (min)</td>
<td>Typically 70 MPa (blind cell); 35 MPa (visual cell) Stirred</td>
</tr>
</tbody>
</table>

For microscopic hydrate experiments techniques, Solid-state NMR spectroscopy, Raman spectroscopy with high pressure windowed cell and X-ray diffraction are widely applied. NMR spectroscopy can delimitate guest occupancy, structure, structural transitions, dynamics, hydration number, hydrate formation and dissociation kinetics. Raman spectroscopy can determine guest occupancy ratios, structure and structural transitions.
X-ray diffraction can specify structure and structure transitions, hydrate crystal growth, decomposition and thermal expansivity\textsuperscript{24}. The Table 2.5 summarizes the techniques. The next Table 2.6 summarizes the techniques according to their measuring capabilities.

### Table 2.6 Techniques presented according to their measuring capabilities\textsuperscript{24}.

<table>
<thead>
<tr>
<th>Capabilities</th>
<th>Technique</th>
<th>Capabilities</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{\text{diss}}, \ T_{\text{diss}}, \ P(t), \ T(t)$</td>
<td>High pressure visual autoclave cell, Rocking cell, Quartz Crystal Microbalance (QCM)</td>
<td>Hydrate phase development vs time (kinetic data)</td>
<td>Solid-state NMR spectroscopy, Raman spectroscopy with high pressure windowed cell, X-ray diffraction (lab/synchrotron)</td>
</tr>
<tr>
<td>Gas consumption rate during growth/decomposition</td>
<td>High pressure visual autoclave cell, Rocking cell</td>
<td>Guest occupancy, structure, structural transitions</td>
<td>Solid-state NMR spectroscopy, Raman spectroscopy with high pressure windowed cell, X-ray diffraction (lab/synchrotron)</td>
</tr>
<tr>
<td>Film growth rate vs time</td>
<td>High pressure visual autoclave cell</td>
<td>Dynamics, hydration number, hydrate formation and dissociation kinetics</td>
<td>Solid-state NMR spectroscopy</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydrate crystal growth, decomposition, thermal expansivity</td>
<td>X-ray diffraction (lab/synchrotron)</td>
</tr>
</tbody>
</table>

### 2.4 Thermodynamic promoters

#### 2.4.1 Hydrate promotion

Hydrate promotion is a new field of study: less than 15 years old. Currently various promoters and mixtures of them are under examination. Promoters (or formers) are classified in two groups: thermodynamic and kinetic. The first ones extend the hydrate formation region in a $P,T$ diagram. Thermodynamic promoters are considered as kinds of ionic liquids (ILs). ILs are organic salts that are generally liquid at room temperatures\textsuperscript{64}. The disadvantage of using these thermodynamic promoters is that the amount of CO$_2$ captured in the hydrate form decreases since the thermodynamic promoters occupy some water cavities\textsuperscript{65}. The most well experimentally examined example is cyclic aliphatic
ether: tetrahydrofuran (THF). THF in water forms nonideal mixture which shows high immiscibility at low-temperatures and complex liquid-phase behavior at high temperature\textsuperscript{66}. THF forms also s(I) structure. Kinetic promoters enhance the hydrate formation rate e.g. sodium dodecyl sulfate (SDS)\textsuperscript{67-69}, dodecyl trimethyl ammonium chloride (DTAC)\textsuperscript{70}.

The selection of appropriate thermodynamic additives is subjected to the potential field of application. Various intermediate sized hydrocarbons have been identified as thermodynamic promoters such as cyclopentane\textsuperscript{65,71}, cyclohexane\textsuperscript{72-74}, neohexane\textsuperscript{75}, propane\textsuperscript{76} are known as heavy hydrate formers. They exhibit low water solubility which is important for desalination or wastewater treatment\textsuperscript{77}. On the other hand, water soluble promoters find attractive application in oil and gas application processes where it is desirable to separate the hydrate promoters from the remaining hydrate formers under atmospheric pressure. Organic substances of that kind are THF\textsuperscript{22,78-98,d}, acetone\textsuperscript{99}, 1,4-dioxane\textsuperscript{92,99} and also tetra-n-butyl ammonium bromide (TBAB)\textsuperscript{100-101}, tetra-n-butyl ammonium chloride (TBAC)\textsuperscript{102,104,105}, tetra-n-butyl ammonium nitrate (TBANO\textsubscript{3})\textsuperscript{16,106}, tetra-n-butyl phosphonium bromide (TBPB)\textsuperscript{107,108}, tetra-iso-amyl ammonium bromide (TiAAB)\textsuperscript{109} and tri-n-butyl methyl ammonium chloride (TBMAC)\textsuperscript{110}.

The Figure 2.9 shows THF+H\textsubscript{2}O hydrate system at equilibrium. It can be readily come out that the use of THF lessens the formation pressure and increase the formation temperature of a hydrate which results in substantially lower operating cost of a process plant.

Some tetra-alkylammonium halides, which are water-soluble, such TBAB, TBAF, TBAC, and so forth, and some tetra-alkylphosphonium halides like TBPB have already been proposed as promoters of gas hydrates. Especially TBAB is generally considered as promising materials for various innovating processes. Because of its high latent heat and suitable temperature of melting, TBAB semi-clathrate hydrate has been proposed as a phase change material (PCM) for cold transport in a novel refrigeration process\textsuperscript{86,110}.

\textsuperscript{d} The authors presented in two articles part of their hydrate equilibrium results for CO\textsubscript{2}+THF+H\textsubscript{2}O systems\textsuperscript{97,98}. 
The phase behavior of tetra-n-butylammonium bromide (TBAB) + water system is rich and complex, as it exhibits vapor-liquid equilibria at low pressures, liquid-liquid equilibria at very high pressures, ion pairing at moderate concentrations, and a complex solid-liquid phase diagram. TBAB forms two types of semi-hydrates: type A (TBAB\(\cdot26H_2O\)) and type B (TBAB\(\cdot38H_2O\)). Type A is formed for concentrations >1.4 mol% and type B exists for lower concentrations. The highest stabilization for type A is achieved on stoichiometric concentration at 3.7 mol% (or 41 wt%). Higher TBAB concentration will cause inhibition effect.

TBAF forms also two types of semi-hydrates: cubic (Css-I) (TBAF\(\cdot29.7H_2O\)) and tetragonal (Ts-I) (TBAF\(\cdot32.8H_2O\)). The transition ofCss-I to Ts-I may occur at >10 MPa and >1.8 mol%. The stoichiometric concentration of TBAF occurs at higher than 2.3 mol% (or 33 wt%). Recently it has been shown that TBAF hydrates are formed two times faster than TBAB hydrates and four times than THF hydrates.
Moreover, the space velocity of the hydrate reactor increases with increasing feed pressure and it is almost two times larger for TBAF than TBAB (13.46 h⁻¹ for TBAB and 25.96 h⁻¹ for TBAF). At higher pressures, for constant temperature, CO₂ concentration in gas phase decreases while in the hydrate phase increases. At higher temperatures,
CO₂ concentration in gas phase increases. The CO₂ amount in CO₂+N₂ hydrates increases greatly with a small increase of CO₂ in vapor phase. Li et al. have used TBAB, TBAC, and TBAF as shown in Figure 2.10, Figure 2.11, and Figure 2.12 respectively.

Another promising promoter seems to be propane (C₃H₈). The system of CO₂/H₂ is presented in Figure 2.13.

Another promoter, which is also a potential phase material for cold storage and transportation in refrigeration and air-conditioning processes, is TBPB. Its capabilities are shown in Figure 2.14. TBPB can store two to four times more CO₂ per H₂O than TBAC and tetra-n-butyl ammonium nitrate (TBANO₃).
Chapter 2

Theory on hydrate promotion

Figure 2.14 CO₂ pressure, \( P_{\text{CO}_2} \), versus temperature, \( T \), H-L-V equilibrium data for the systems \( \text{CO}_2+\text{H}_2\text{O} \)\(^{76,122}\) and \( \text{CO}_2+\text{TBPB}+\text{H}_2\text{O} \)\(^{121}\).

Cyclopentane (CP) is also a potential promoter. CP is water immiscible cyclic hydrocarbon. The merits of CP over THF and TBAB can be concluded to the following three statements\(^{65}\):

\( \text{a)} \) the melting point of CP hydrates is higher than that of THF hydrates

\( \text{b)} \) CP is less toxic than THF and

\( \text{c)} \) the equilibrium pressure of CP+CO₂ binary hydrates is independent of CP concentrations due to immiscibility of CP + water.

In addition, the hydrate formation rate with CP/water emulsion is higher than that of CP aqueous solution due to the larger contact area of gas and liquid which controls hydrate formation rate\(^{71}\).

Quite recently, mixture of promoters (THF and CP) has been tested\(^{22}\). The following Figure 2.15 shows four-phase equilibrium of CP+THF+H₂O and CP+H₂O hydrate.
system\textsuperscript{22}. It presents the significant reduction in equilibrium pressures caused by the addition of 4 wt\% THF to the aqueous phase (CP and water). It can readily come out the synergetic effect of promoters’ mixture, namely THF and CP which lessen the formation pressure and increase the formation temperature of hydrates\textsuperscript{111}. CO\textsubscript{2} hydrate formation systems are also presented in Appendix A, Figures A.1 and A.2.

![Figure 2.15](image)

\textbf{Figure 2.15} Four-phase (H-L\textsubscript{w}-L\textsubscript{s}-V) equilibrium pressures (absolute) as functions of temperature for mixed hydrates of CP/THF/CO\textsubscript{2}. Hydrates formed from a two-liquid phase system prepared from an aqueous solution containing 4 wt\% THF and an organic phase containing pure CP. For comparison, (H-L\textsubscript{w}-L\textsubscript{s}-V) hydrate equilibrium data exhibiting a mixed CP/CO\textsubscript{2} hydrate phase of the ternary system \{H\textsubscript{2}O + CP + CO\textsubscript{2}\} are included. The initial vapor phase consists of pure CO\textsubscript{2} in both cases. (\textbullet) CP/THF/CO\textsubscript{2}, Herslund \textit{et al.}\textsuperscript{22}, (\textblacksquare) CP/CO\textsubscript{2}, Herslund \textit{et al.}\textsuperscript{22}.

Finally, there are also kinetic promoters which are only used to accelerate hydrate formation and have no impact on formation thermodynamics. In this work, kinetic promoters have not been used. Most examined examples of this category are sodium dodecyl sulfate (SDS), Figure 2.16, biorfuctants\textsuperscript{123} or minerals\textsuperscript{11,12}. SDS is a surfactant which can effectively reduce the interfacial tension of gas-liquid contact and accelerate the rate of gas hydrate formation\textsuperscript{124,125}. Another kinetic promoter, which is currently under examination, is silica gel\textsuperscript{60,126,127}. Silica gels with a nominal diameter of 100.0 nm have
exhibited increased gas consumption during gas hydrate formation, suggesting higher conversion of water into gas hydrate\textsuperscript{60}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.16.png}
\caption{CO$_2$ H-LW-V equilibrium curves for pure water, 500 ppm SDS and 5mol\% THF and induction point for THF 5 mol\%, SDS- 500ppm and SDS-500ppm/THF-5mol\%. Sources: no additive; SDS-500ppm, THF 5 mol\%, THF- induction, SDS-induction and SDS/THF induction\textsuperscript{124}.}
\end{figure}

2.4.2 Critically Reviewed PT diagrams for CO$_2$ + promoter systems + H$_2$O

A sequence of $P,T$ Figures of CO$_2$+THF/TBA Halides +(other gas)+H$_2$O are presented so that a more in depth view of most of the available literature results in CO$_2$ hydrate promotion can be acquired. All compositions are given in mol fractions. The first $P,T$ Figure 2.17 shows CO$_2$+THF+H$_2$O system at various concentrations. An article of CO$_2$+H$_2$O equilibrium\textsuperscript{128} is added for comparison purposes in order to show the promotion effect of every chemical. Most of the results agree very well with each other, especially at lower pressures, but there are some discrepancies at higher pressures, e.g. above 2 MPa. The red square (■) and blue (Ж) markers that correspond to 1% THF from Shin et
al. and Seo et al. respectively seem to be slightly inconsistent. In conclusion, the results from different authors are in good agreement with each other.

![Figure 2.17](image)

**Figure 2.17** CO₂+THF+H₂O system. For clarity reasons, the systems are presented by two numbers in brackets. The first number denotes the mol fraction of CO₂ of a potential binary gas mixture and the second one denotes the promoter concentration. References are presented according to their presence in figure from left to right.

The next Figure 2.18 depicts P,T equilibrium points of the system CO₂+CH₄+TBAB+H₂O at various concentrations. As shown previously, an article of CO₂+CH₄ equilibrium with pale blue cross (+) marker is added for comparison purposes. The blue rhombus (◆) and filled orange circle (●) markers of Acosta et al. and Mohammadi et al. respectively that correspond to 40% CO₂ and 0.29% TBAB mol fractions are in good accordance. The
rest systems have different compositions which prohibits further comparison. Nevertheless, there is consistency in the fact that as TBAB concentration increases, the promotion effect becomes more significant. In conclusion, the results from different authors are in very good agreement with each other.

The Figure 2.19 represents the system CO$_2$+H$_2$+TBAB+H$_2$O at various concentrations. The points marked with green triangle (▲), a green dash (●), a filled orange circle (+) and purple cross (♦) markers show CO$_2$+H$_2$ systems for comparison purposes. The purple
cross (+) markers of Li et al.\textsuperscript{102} shows CO\textsubscript{2}+H\textsubscript{2}+H\textsubscript{2}O system as well but it does not appear correct because for the low CO\textsubscript{2} concentration being used, the results should have been located at higher pressures. The filled green circle square (●) and (xes) markers of Li et al.\textsuperscript{102} and Kim et al.\textsuperscript{57} respectively, that correspond to app. 40\% CO\textsubscript{2} and app. 3\% TBAB coincide excellently. Moreover, from the same authors, the blue (xes) and the pale green triangle (▲) markers that correspond to app. 40\% CO\textsubscript{2} and 0.5\% TBAB are in very good agreement. In addition, the red (xes) and pale purple (xes) markers of the same authors that correspond to app. 40\% CO\textsubscript{2} and 1\% TBAB are in very good agreement. In conclusion, the results from different authors are in good agreement with each other.

In general, the concentrations below 1 mol\% TBAB of Li et al.\textsuperscript{102}, the filled orange circle (●) markers of Mohammadi et al.\textsuperscript{61} for CO\textsubscript{2}+H\textsubscript{2}+H\textsubscript{2}O system and purple cross (+) markers for the same system of Li et al.\textsuperscript{102} seem to be problematic concerning visual observation.

Figures 2.20, 2.21 and 2.22 show CO\textsubscript{2}+TBAR+H\textsubscript{2}O systems where R is bromide, chloride or fluoride anion accordingly. In Figures 2.20 for CO\textsubscript{2}+TBAB+H\textsubscript{2}O systems, the purple (xes) and the pale blue (◆) rhombus markers of Lee et al.\textsuperscript{11} and Li et al.\textsuperscript{104} respectively that corresponds to app. 0.6\% TBAB are in good agreement. In addition, the pale purple (xes) and the red dash (-) markers of Lin et al.\textsuperscript{118} and Mohammadi et al.\textsuperscript{50} respectively that correspond to app. 0.29\% TBAB are in good agreement. In addition, the green dash (-) and triangle (▲) markers of Lin et al.\textsuperscript{118} and Mohammadi et al.\textsuperscript{50} respectively that correspond to app. 0.6\% coincide excellently. A TBAB concentration of 2.7 mol\% (stoichiometric) proves to be the most efficient. Above that concentration inhibition effect is observed as it is shown by the filled orange circle (●) of Lee et al.\textsuperscript{11}, orange dash (-) of Ye and Zhang\textsuperscript{131} and pale blue (xes) of Mohammadi et al.\textsuperscript{50}. 
Figure 2.19 CO₂+H₂+TBAB+H₂O system. For clarity reasons, the systems are presented by two numbers in brackets. The first number denotes the mol fraction of CO₂ in CO₂+H₂ gas mixture and the second one denotes the promoter concentration. References are presented according to their presence in figure from left to right.
The TBAC results are not sufficient for safe conclusions. Nonetheless, the red square (■) markers of Makino et al.\textsuperscript{105} and the pale red (Ж) markers of Mayoufi et al.\textsuperscript{14}, that correspond to app. 2.3 mol\%, are in very good agreement. In addition, the green triangle (▲) markers of Mohammadi et al.\textsuperscript{13} and the pale blue (●) markers of Li et al.\textsuperscript{104}, that correspond to app. 0.3 mol\%, are in very good agreement.

**Figure 2.20** CO$_2$+TBAB+H$_2$O systems. For clarity reasons, the systems are presented by two numbers in brackets. The first number denotes the mol fraction of CO$_2$ of a potential binary gas mixture and the second one denotes the promoter concentration. References are presented according to their presence in figure from left to right.
The TBAF results are presented in Figure 2.22. The results are not sufficient for safe conclusions but there is consistency in the fact that as TBAF concentration increases, the promotion effect becomes more significant. Moreover, TBAF achieves the maximum promotion effect compared to TBAB and TBAC at similar concentrations according to Li et al.\textsuperscript{104}.
Finally, in Figure 2.23 and 2.24 the systems CO₂+CP+H₂O and CO₂+CH₄+THF+H₂O are investigated by two authors respectively. Their results coincide completely in both cases at same concentrations.

![Figure 2.23 CO₂ + CP + H₂O system.](image1)

![Figure 2.24 CO₂ + CH₄ + THF + H₂O system.](image2)

### 2.5 Conclusions

In this chapter, an overview of hydrate structures, hydrate measuring techniques together with hydrate promoter systems were reviewed. The chapter presented the theoretical background on hydrate promotion which is necessary for the next chapters. Moreover, the final section presented an overview of the available $P,T$ equilibrium data on CO₂ hydrate promotion. The available literature is insufficient on CO₂+N₂ gas mixture which is a common effluent in oil and gas industry\textsuperscript{10}. Moreover, TBAC and TBAF promoters are lacking in experimental data. Therefore, the next chapter presents equilibrium data for CO₂+N₂ gas mixture with the use of promoters using gas mixtures of low CO₂ concentration to simulate real systems. The TBAB, TBAF and CP promoters were examined adding new data to the available literature.
Experimental methodology

The indwelling of God (in us) is to have foundations of God via memory. In such way we become temple of God when the continuance of memory (of God) is not paused by earthy concerns, when the mind is not disturbed by unexpected passions but (instead when) the pious (mind) avoids everything, he departs to God and he dwells in things that leads to virtue by expelling the provocations towards us for evilness.

St. Basil the Great (329 – 378 AD)
In this chapter the calibration of transducers, the experimental setup, the measuring procedure and the hydrate equilibrium results are presented and discussed. The results are produced using TBAB, TBAF, CP promoters and mixtures of them. The combination of TBA salts and CP was inspired by Li et al.\textsuperscript{134} and Herslund\textsuperscript{20,22}. The results confirm that synergetic effect between TBA salts and CP indeed occurs which decreases further the hydrate equilibrium pressure at specific $P,T$ conditions and aqueous concentrations. This chapter is published in peer-review journals of Fluid Phase Equilibria and Chemical and Engineering Data as shown in Appendix E.

3.1 Equipment used

3.1.1 Calibration of pressure and temperature transducers

The temperature probe was carefully calibrated against a 25-$\Omega$ reference platinum resistance thermometer (TINSLEY Precision Instruments). The 25-$\Omega$ reference platinum resistance thermometer was calibrated by the Laboratoire National d’Essais (LNE, Paris) based on the 1990 international temperature scale (ITS90). The equilibrium pressure is measured using two calibrated pressure transducers (GE UNIK 5000).

![Graph showing absolute uncertainty of pressure transducer for 0-10 bar.](image1)
Two pressure transducers of 10 bar and 100 bar were calibrated. The accuracy was found to be ±0.004 bar and ±0.015 bar for 10 bar and 100 bar accordingly as shown in Figures 3.1 and 3.2. For the temperature transducer, the accuracy was found to be ±0.02 K as presented in Figure 3.3.

**Figure 3.2** Absolute uncertainty of pressure transducer for 0-100 bar.

**Figure 3.3** Absolute uncertainty of temperature transducer.
The 2\textsuperscript{nd} degree parameters ($X_{\text{cal}} = a \cdot X_{\text{read}}^2 + b \cdot X_{\text{read}} + c$) used for the temperature and pressure correction are shown in Table 3.1.

<table>
<thead>
<tr>
<th>Pressure range (bar)</th>
<th>Pressure parameters (2\textsuperscript{nd} degree)</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-20</td>
<td>$a = -3.34E-05$, $b = 1.00075659$, $c = -0.00029732$</td>
<td>±0.015 bar</td>
</tr>
<tr>
<td>20-70</td>
<td>$a = -1.31E-05$, $b = 1.00248668$, $c = -0.05910184$</td>
<td>±0.015 bar</td>
</tr>
<tr>
<td>0-100</td>
<td>$a = -6.87E-06$, $b = 1.00051235$, $c = 0.07324214$</td>
<td>±0.015 bar</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature parameters (2\textsuperscript{nd} degree)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.19E-05</td>
</tr>
</tbody>
</table>

### 3.1.2 Calibration of Gas Chromatograph

The first gas mixture (e.g. 6.87/93.13 mol\% CO\textsubscript{2}/N\textsubscript{2}) was produced and then measured with a gas chromatograph (Varian, CP3800). At first, the GC detector (TCD) was calibrated for CO\textsubscript{2} and then for N\textsubscript{2}, Figures 3.4 and 3.5 respectively. Similar calibration plots created for the other three gas mixtures.

![Figure 3.4](image-url) CO\textsubscript{2} volume error against peak area as measured with GC.
Figure 3.5 N₂ volume error against peak area as measured with GC.

From the area of the peak measured for specific CO₂ or N₂ volumes, which for that case syringes (connected with eVol® Automated Analytical syringe, SGE Analytical Science) of 500μl and 100μl were used, a 2nd order polynomial expression ($n_{cal}=a \cdot S^2+b \cdot S+c$) was derived for each gas at specific range of CO₂ and N₂ concentrations. The polynomial parameters for the first gas mixture are shown in Table 3.2.

<table>
<thead>
<tr>
<th>Gases</th>
<th>Range (μl)</th>
<th>Composition parameters of 2nd degree polynomial</th>
<th>Uncertainty (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>0 – 100</td>
<td>1.56E-13, 4.64E-09, 2.64E-08</td>
<td>±1.0</td>
</tr>
<tr>
<td>N₂</td>
<td>100 – 500</td>
<td>-6.18E-14, 5.49E-09, 2.27E-07</td>
<td>±0.6</td>
</tr>
</tbody>
</table>

3.2 Hydrate equipment description

A brief sketch of the experimental equipment is presented in Figure 3.6. First of all, there are two gas cylinders one of nitrogen and one of mixture of CO₂ and N₂. The first is used for cleaning the cell and the last for providing the gas mixture at desirable pressure. Then there is a vacuum pump to avoid contamination of the tube and to help cleaning the cell.
The cell is immersed in a water bath for controlling the temperature and three sensors are attached to it; two of temperature (on the top and bottom of the cell) and one of pressure on the top. All of them are connected after acquisition units to personal computer. The temperatures are determined by the temperature transducer of the top and pressure transducer of the bottom.

![Simplified schematic diagram of equilibrium cell equipment. LNP: liquid nitrogen container. VP: vacuum pump. SD: stirring device. TR: temperature regulator. TT: temperature transducer bottom. PT: pressure transducer top. DAU: data acquisition unit.](image)

**Figure 3.6** Simplified schematic diagram of equilibrium cell equipment. LNP: liquid nitrogen container. VP: vacuum pump. SD: stirring device. TR: temperature regulator. TT: temperature transducer bottom. PT: pressure transducer top. DAU: data acquisition unit.

Figures 3.7, 3.8 and 3.9 show photos of the experimental setup. The cylinder of the CO₂/N₂ mixture is shown in Figure 3.7. Temperature of the cell is controlled using a thermostatic water bath (LAUDA PROLine RP3530). One platinum temperature probe (Pt100) inserted in the cell interior is used to measure the temperature inside the cell within measurement accuracies, which are estimated to be less than 0.02 K with a second order polynomial calibration equation. The data acquisition units (Agilent 34970A, HP 34970A) are coupled with a personal computer to measure and automatically record pressure, temperature and time data. The data acquisition software also allows adjusting the rate of data acquisition, Figure 3.8. Continuous recording of pressures and...
temperatures allows detecting any subtle changes in the system and true equilibrium conditions.

Figure 3.7 Cylinder of CO₂ and N₂ gas mixture.

A motor-driven turbine agitation system (Top Industrie, France) enables to stir the cell contents at a speed up to 2000 rpm to increase the fluids contact and enhance water conversion into hydrate, Figure 3.9.
3.2.1 Measuring procedure

The four gas mixtures used in this work were prepared thanks to a gas cylinder in which different concentrations of CO₂ and N₂ were utilized. The CO₂ and N₂ gas bottles used in this work were supplied by Air Liquide. The molar fractions of CO₂ were app. 0.15, 0.11, 0.07 and 0.005.

<table>
<thead>
<tr>
<th>Product Name</th>
<th>Abbreviation</th>
<th>CAS-number</th>
<th>Purity</th>
<th>Supplier</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>CO₂</td>
<td>124-38-9</td>
<td>99.998 (vol%)</td>
<td>Air Liquide</td>
<td>gas</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N₂</td>
<td>7727-37-9</td>
<td>99.999 (vol%)</td>
<td>Air Liquide</td>
<td>gas</td>
</tr>
<tr>
<td>Tetra-n-butylammonium bromide</td>
<td>TBAB</td>
<td>1643-19-2</td>
<td>≥99+%</td>
<td>Acros Organics</td>
<td>solid</td>
</tr>
<tr>
<td>Tetra-n-butylammonium fluoride</td>
<td>TBAF</td>
<td>429-41-4</td>
<td>75 wt% in H₂O</td>
<td>Sigma Aldrich</td>
<td>liquid</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>CP</td>
<td>287-92-3</td>
<td>≥98%</td>
<td>Acros Organics</td>
<td>liquid</td>
</tr>
</tbody>
</table>
The exact concentration was measured by the gas chromatograph (see section 3.1.2). TBAB solutions with mass fractions of (0.05, 0.10 and 0.20) and TBAF solutions with mass fractions of (0.03, 0.05 and 0.10) were prepared by gravimetric method using an accurate analytical balance (Mettler, AT200), with mass accuracy of ±0.0001g. Double-distilled and deionized water from Direct-Q5 Ultrapure Water Systems (MilliporeTM), was used in all experiments. When needed, cyclopentane was added in TBAB and TBAF solutions with use of proper syringes. The chemicals used are presented in Table 3.3.

The schematic diagram of the experimental apparatus employed for measuring hydrate phase equilibrium points in this work is shown in Figure 3.6. Isochoric temperature trace method is applied. There are two cylinders, one of nitrogen gas and one of CO₂ and N₂ gas mixture. The first one is used for cleaning the Equilibrium Cell (EC) and the other one for providing the gas mixture at desirable pressure. The EC is immersed in a water bath for controlling the temperature. The EC temperature is controlled using a thermostatic water bath (LAUDA PROLine RP3530). Two platinum temperature probes (Pt100, JM6081) inserted in the cell interior—at the top (gas phase) and the bottom (liquid phase)—are used to measure the temperature inside the EC within measurement absolute uncertainties, which are estimated to be less than $u(T, k = 2) = 0.02$ K. All of them are connected after acquisition units to personal computer. The results are calculated by the platinum probes of the top and the pressure transducer of the bottom. The pressure in EC is measured using a UNIK 5000 GE absolute pressure transducer with an absolute uncertainty of $u(P, k = 2) = 0.0015$ MPa.

More specifically, the main part of the setup is the EC which is immersed in thermostatic water bath (LAUDA PROLine RP3530) containing double-distilled and deionized water. The EC is made of the 316 stainless steel; its maximum working pressure and its inner volume is 40 MPa and 125 mL respectively. A motor-driven turbine agitation system (Top Industrie, France) enables to stir the cell contents at a speed up to 1200 rpm to increase the fluids contact and enhance water conversion into hydrate. For calibrating temperature and pressure uncertainties second order polynomial calibration equation was used (see section 3.1.1). The data acquisition units (Agilent 34970A, HP 34970A) were coupled with a personal computer to measure and automatically record (every 25s) pressure,
temperature and time data. The data acquisition software also allows adjusting the rate of data acquisition. Continuous recording of pressures and temperatures allows detecting any subtle changes in the system and true equilibrium conditions.

After careful evacuation of the EC using the vacuum pump (Oerlikon leibold vacuum, Trivac D2.5E) for two days, 15-40 ml of promoter solution (TBAB, TBAF, CP, TBAB+CP, TBAF+CP) that is about 20-30 vol% of EC was subsequently filled with aqueous solution and then the gas mixture was introduced in the EC from the cylinder. All amounts of substances supplied to the cell were quantified. Pressure and temperature measurements under hydrate stability conditions were carried out as follows: The cell was immersed into the temperature-controlled bath and temperature was decreased to form hydrates, while agitating at a constant speed of about 1070 rpm to increase the fluids contact and enhance water conversion into hydrate.

The temperature of the system was kept constant for at least 7h to overcome the metastable period and to allow complete hydrate formation, which was detected by a noticeable pressure drop. Temperature was then increased step-wisely at rate of about 0.4 °C/h. At every temperature step, temperature was kept constant until temperature and pressure were established. The stabilization time needed fluctuates from 1h 15 min to 1h 30 min as gas pressure increases from 10 to 80bar. As implemented by Ohmura et al., a pressure-temperature diagram was obtained for each experimental run from which the hydrate dissociation condition could also be determined. For measuring an equilibrium condition at a higher pressure, the pressure of the system was increased by successively supplying gas mixture to the equilibrium cell until achieving the desired pressure. In this way, several $P, T$ equilibrium data were obtained from each experimental run. Pressure and temperature accuracies for transducers were 15 mbar and 0.02 °C respectively.
After two days, a $P,T$ diagram was produced, as shown for 20% TBAB and CO$_2$/N$_2$ 6.87/93.13 in Figure 3.10. The procedure is as follows. At first, the cell was cooled up to 2 °C (from A to $\Gamma$). After staying at least 10h at this point equilibrium was achieved which means that hydrates were fully formed. The next day dissociation started. The temperature was increased rapidly (from $\Gamma$ to $\Delta$) and then step-wisely so that every temperature step corresponded to hydrate equilibrium dissociation points (from $\Delta$ to A). Finally, the dissociation point is calculated by the intersection of the HVL polynomial line with the VL equilibrium line (see also chapter 4.1).

**3.3 Hydrate equilibrium results**

**3.3.1 TBAB results**

The TBAB results for CO$_2$+N$_2$ mixture concentrations are summarized in Figure 3.11. The results are compared with literature data. At first, for comparison purposes, the unpromoted system CO$_2$+N$_2$ is reported$^{136}$. In general, it is observed good agreement of results of this work with the literature data for similar systems of 5%, 10% and 20 wt% TBAB solutions which correspond to 0.29%, 0.62% and 1.38 mol% respectively. For clarity reasons, the systems are presented by two numbers in brackets.
Figure 3.11 Hydrate dissociation points for different systems using TBAB as promoter. The Figure contains systems of this work and systems of CO₂+N₂+TBAB+H₂O from literature. For clarity reasons, the systems are presented by two numbers in brackets. The first number denotes the mol fraction of CO₂ in CO₂+N₂ gas mixture cylinder and the second one denotes the promoter concentration. Black markers connected with trendlines correspond to results of this work. References are presented according to their presence in figure from left to right.

The first number denotes the mol fraction of CO₂ in CO₂+N₂ gas mixture cylinder and the second one denotes the promoter concentration expressed in mol%. Black markers connected with trendlines correspond to results of this work. From Gibbs phase rule, the parameters that suggest where the equilibrium lines should be located are the gas mixture concentration, the promoter concentration in aqueous solution and the gas-to-liquid ratio (mol/mol). For simplicity reasons and owning to the fact that gas-to-liquid ratio is not always mentioned in literature, it was omitted from this study.
In general, the higher the CO₂ in CO₂+N₂ gas mixture concentration, the more on the right of the \( P,T \) diagram the hydrate dissociation results are located. This results in further decreasing of hydrate formation pressure. At higher temperatures, CO₂ is captured easier than N₂. In modeling, the analogy of Langmuir absorption approximates successfully hydrate crystallization (see chapter 5). So, the size and the kinetic energy of CO₂ at higher temperatures enhance more CO₂ capture than N₂ capture.

The results of similar promoter and gas mixture concentrations are in excellent agreement, e.g. with (14.92, 0.29) from this work, with (13.70, 0.29)\textsuperscript{138}, with (20, 0.29)\textsuperscript{139} and with (15, 0.29)\textsuperscript{132}. Another observation is that the system of (6.87, 0.62) of this work is approximately placed on the left of (20, 0.62)\textsuperscript{139} which shows that CO₂ hydrates are formed at lower pressures than N₂ hydrates.

Similarly, for higher TBAB concentrations, the results of similar promoter and gas mixture concentrations are in good agreement, e.g. with (6.87, 1.38) from this work, with (20, 1.38)\textsuperscript{139}. According to the literature, there is mismatch of (13.70, 0.29)\textsuperscript{138} with the system (15.9, 0.29)\textsuperscript{84} respectively as shown in Figure 3.10.

For a more detailed comparison of results of this work, Figures 3.12 and 3.13 include systems of this work and for CO₂ or N₂ plus TBAB+H₂O from literature respectively. In Figure 3.12 the results of this work are located between the system of pure CO₂ hydrate and systems of CO₂+TBAB+H₂O from literature. This is expected due to the high content of N₂ that was used in results of this work. The results from literature are smoothly shifted to the right-hand side of the diagram as TBAB concentration increases. In Figure 3.13, results of this work are located between systems of N₂+TBAB+H₂O from literature. This is expected because of the high content of N₂ in the gas mixture used. Specifically, the system of (11.24, 0.29) of this work is located as expected on the right side of the systems of (0.0, 0.29)\textsuperscript{11} and (0.0, 0.29)\textsuperscript{50}. 

Experimental uncertainties and consistency analysis of results

Chapter 4

Figure 3.12 Hydrate dissociation points for different systems using TBAB as promoter. The Figure contains systems of this work and systems of CO₂+TBAB+H₂O from literature. For clarity reasons, the systems are presented by two numbers in brackets. The first number denotes the mol fraction of CO₂ in CO₂+N₂ gas mixture and the second one denotes the promoter concentration. Black markers connected with trendlines correspond to results of this work. References are presented according to their presence in figure from left to right.

The system of (6.87, 1.38) of this work coincides well with the results of (0.0, 2.59)\textsuperscript{11} which reveals that the addition of 6.87\% of CO₂ in pure N₂ counteracts the additional use of 2.21 mol\% TBAB in aqueous solution, which is the deduction of 2.59 mol\% and 1.38 mol\% of the two systems.
Chapter 4  
Experimental uncertainties and consistency analysis of results

Figure 3.13 Hydrate equilibrium points for different systems using TBAB as promoter. The Figure contains systems of this work and systems of N₂+TBAB+H₂O from literature. For clarity reasons, the systems are presented by two numbers in brackets. The first number denotes the mol fraction of CO₂ in CO₂+N₂ gas mixture cylinder and the second one denotes the promoter concentration. Black markers connected with trendlines correspond to results of this work. References are presented according to their presence in figure from left to right.

3.3.2 Results for CP as promoter

Similar procedure is followed for the system CO₂+N₂+CP+H₂O. For CO₂/N₂ mixture (6.87/93.13), 15 ml and 25 ml of CP aqueous solution of 20 wt% (6.03 mol%) and 52.57 wt% (22.15 mol%) were prepared respectively. The stoichiometric concentration of CP in the solution for s(II) hydrates is 18.65 wt% (5.56 mol%)\textsuperscript{140}. For CP concentrations >27.80 wt%, according to Galfré et al.\textsuperscript{141}, emulsion system is produced. For \(P, T\) measurements,
stirring velocity is not of importance. It was used relatively high stirring velocity (1070 rpm). It came out that results of this work were similar for both CP concentrations used. Figure 3.14 summarizes the results.

In phase equilibrium a mixture may exist between the simple CO₂ hydrate in s(I) and double CO₂-CP hydrates in s(II)¹⁵. In Figure 3.14, there is a region in which CO₂+N₂ mixture dissociation points should exist based on experimental results⁷²,⁷³,¹³³. These are the boundaries of pure CO₂ and pure N₂ plus CP+H₂O systems respectively. The results of this work are included in these boundaries. Another observation is that CP does not ‘‘sense’’ the small mol fraction of CO₂ (e.g. 6.87 mol%) of CO₂ in CO₂+N₂ gas mixture.
In other words, most probably N₂ is predominantly captured –higher N₂ selectivity– rather than CO₂ since the results between pure N₂ and CO₂+N₂ are identical. According to results of this work and literature⁶⁵, the CP concentration does not have any significant impact on the thermodynamic equilibrium in contrast with TBAB due to water immiscibility in cyclopentane. This occurs for both the emulsion and the non-emulsion CP case. In other words, the two systems of different CP concentrations match each other excellently. Very recently it was observed that the decrease in pressure equaled the increase in temperature for the hydrate phase equilibrium¹⁴³. The improvement in the hydrate phase equilibrium temperature produced by CP was limited to ~12 K and the hydrate stability temperature was not increased further when the mol concentration of CP was >1%¹⁴³. The effects of CP on the CO₂ hydrate phase equilibrium conditions can be explained by the theory of hydrate crystalline structure²⁴. Typically, CO₂ can easily enter the large cavity (5₁₂6²) of an s(I) hydrate and the small cages of 5₁₂ in the presence of other hydrate formers. CP helps to form double s(II) hydrates with CO₂. The large cavity (5₁₂6⁴) of a s(II) hydrate is occupied by CP and the smaller cavity (5₁₂) is filled with CO₂. The precipitous shift in the CO₂ hydrate phase equilibrium curve is caused by a hydrate crystal change from s(I) (pure CO₂) to s(II) (with the presence of CP)¹⁴³. As the crystal structure changes, a different thermodynamic state (i.e. three-phase temperature and pressure) is required for stability. Small amount of CP encourages the stability of s(II), the occupation of CO₂ in the 5₁₂ cavities and provides the large degree of stability to the s(II) large cage. The change in hydrate structure can elucidate in a molecular level the substantial decrease in the hydrate phase equilibrium pressure that is required for a small composition change¹⁴³.

3.3.3 TBAF results

The TBAF results for CO₂+N₂ gas mixture global concentrations are summarized in Figure 3.15. The results are compared with literature data. At first, for comparison purposes, the unpromoted system N₂+H₂O is reported¹⁴⁴. In general, it is observed good agreement of results of this work with the literature data for similar systems of 5% and 10
wt% TBAF solutions which correspond to 0.36% and 0.76 mol% respectively. For 3 wt% TBAF solution no data from literature were found.

**Figure 3.15** Hydrate dissociation points for different systems using TBAF as promoter with CO₂ + N₂ (0.48/99.52) gas mixture. References are presented according to their presence in figure from left to right. The first number denotes the mol fraction of CO₂ in CO₂+N₂ gas mixture cylinder and the second one denotes the promoter concentration used in this work. Black markers connected with trendlines correspond to results of this work. References are presented according to their presence in figure from left to right.
For clarity reasons, the systems are presented by two numbers in brackets. The first number denotes the mol fraction of CO₂ in CO₂+N₂ gas mixture cylinder and the second one denotes the promoter concentration expressed in mol%. Black markers connected with trendlines correspond to results of this work. From Gibbs phase rule, the parameters that suggest where the equilibrium lines should be located are the gas mixture concentration, the promoter concentration in aqueous solution and the water-to-gas ratio (mol/mol). For simplicity reasons and owning to the fact that gas-to-liquid ratio is not always mentioned in literature, it was omitted from this study.

The results for 3.2%, 5% and 10 wt% TBAF, which correspond to 0.23 mol%, 0.36 mol% and 0.76 mol% respectively, seem well placed in the Figure 3.15. The gas mixture, which is 99.52% mol N₂, produced steeper results than with higher CO₂ concentration. In addition, 0.36 mol% TBAF are in good agreement with similar solutions from literature¹⁴,⁹⁰,¹³², even though the last correspond to pure N₂ results.

### 3.3.4 Mixtures of TBAB+CP and TBAF+CP

In Figure 3.16, three systems of this work for mixture of TBAB+CP and systems from literature¹³²,¹³⁹ for similar conditions, e.g. CO₂ in CO₂+N₂ and TBAB solution concentrations, are presented. In the caption of Figure 3.17, along with the two numbers in brackets, there is a third number denoting CP addition in TBAB solution in vol%. The addition of 5 vol% CP in TBAB have shown that for TBAB 1.38 mol%, there is synergetic effect between TBAB and CP which means that the results are better when CP is added compared to pure TBAB. The effect is more significant for P > 2.5 MPa as shown in Figure 3.16. When TBAB 0.62 mol% fraction is used, the results of TBAB and CP proved to be identical with those of pure promoter at same concentration.
For TBAB 0.29 mol% with CP 5 vol%, the gas systems used in this study are different but it is highly improbable that the change in CO₂ concentration would have such a drastical impact on thermodynamic equilibrium that could induce promotion.

Finally, in Figure 3.17 all hydrate dissociation points of this work for TBAF promoter are presented. The use of CP in 0.76 mol% TBAF has no effect in the results compared to pure TBAF results of 0.76 mol% while for 0.36 mol% TBAF the behavior is mixed when CP is present. For low pressures (<30 bar), inhibition effect is observed while for higher pressures (>30 bar) promotion effect appears.
Another reason for the promotion enhancement could be attributed to the fact that there seems to be some connection between the synergetic effect, the molecular weights and hydrate structures of TBA salts. TBAF is 23% lighter than TBAB and requires 0.26 times (which is the ratio of 0.36/1.38) lower molar concentration so that a synergy between TBAB or TBAF and CP may occur. For the TBAB, it is known that there is phase transition from type B to type A at \(~18\) wt\% (1.21 mol\%)\textsuperscript{90,94}. TBAF has also two crystal structures: a tetragonal TBAF\(\cdot\)32.8H\(_2\)O and a cubic TBAF\(\cdot\)29.7H\(_2\)O at which the phase transition from tetragonal to cubic occurs at \(~33\) wt\% (3.3 mol\%)\textsuperscript{145}. Moreover, fluoride is more electronegative anion than bromide. These facts might play some role in promotion enhancement.
3.4 Conclusions

Hydrate equilibrium points for CO₂ and N₂ were measured with the use of tetra-n-butylammonium bromide (TBAB), tetra-n-butylammonium fluoride (TBAF), cyclopentane (CP) and mixtures of TBAB and TBAF with CP. The use of higher TBAB concentration (1.38 mol%) and CP (5 vol%) revealed promotion effect and as the pressure rises (>3.5 MPa), the phenomenon becomes more intense as presented in Figure 3.16. In addition, the higher the CO₂ concentration, the stronger the promotion is for every concentration of TBAB aqueous solution. On the contrary, the results have shown that the simultaneous use of TBAB (0.29 mol%) and (0.62 mol%) with CP (5 vol%) did not have any impact on thermodynamic equilibrium. For the system TBAB (0.29 mol%) with CP (5 vol%), even though the gas mixture systems are different, it is rather unlikely that there is positive impact on promotion. However, this fact is not easily observable for low differences of CO₂ concentration in mixtures. Consequently, it came out that the factor of gas mixture concentration has moderate impact for TBAB on hydrate equilibrium points compared to promoter’s concentration. All the results of this work are presented in Figure 3.18.

The use of CP solution (even though it is virtually water insoluble) proved to be stronger promoter than TBAB maybe because of the different hydrate structure it induces. According to the hydrate promotion ability of TBAB for 40 wt% (3.60 mol%) TBAB, above of which it acts as inhibitor, the promotion results may become similar to CP results. The stoichiometric concentration of CP in the solution for structure II hydrates is 18.65 wt% (5.56 mol%) when higher CP concentration than was used, e.g. 52 wt% (22.15 mol%), the results showed slight inhibition effect.
Finally, TBAF proved to be by far much stronger promoter than TBAB and CP, especially for lower pressures. This is not easily observable because of the almost pure N\textsubscript{2} mixture it was used. The use of TBAF concentration (0.36 mol%) with CP (5 vol\%) revealed...
promotion effect above 30 bar and as the pressure rises it becomes more intense. Moreover, the gas composition used in TBAF promotion has minor impact on equilibrium results compared to TBAB promotion.

In general, classical gas hydrates generally form at high pressures and/or low temperatures. Flue gas of power stations is emitted in low pressures and high temperatures. The promoters’ examined like TBAB, TBAF, CP can enable hydrate formation at conditions close to ambient pressure and lower temperatures (5 - 10 K) above the normal ice-point of water in constrast to non-promoted systems. The drawbacks of using CP are its high volatility and its hazard towards environment. Furthermore, CP lowers the selectivity towards carbon dioxide in the hydrate phase compared to the unpromoted system as this study has shown. On the other hand, TBA salts are environmental friendly but they exhibit low gas uptake due to their unique semi-clathrate structure. Moreover, their promoting capabilities are lower than CP and as this study has shown their ability depends significantly on the initial CO₂ gas content.
Experimental uncertainties and consistency analysis of results

Στερεότητα νοὸς ἐστὶ μετεωροσκοπία τῶν νοητῶν, ἣτις ἀμιλλάται τῇ ουρανίῳ χροίᾳ, ἐφ’ ἣ διαυγάζει ἐν τῷ καιρῷ τῆς προσευχῆς τὸ φῶς τῆς ἁγίας Τριάδος.

Ἅγ. Εὐάγριος ὁ Ποντικός (345 – 399 μ.Χ.)

1 Firmness of mind is observatory of perceptible, which contend with the heaven skin, upon which illuminates at the time of praying the light of Holy Trinity.

St. Evagrius of Pontus (345 – 399 AD)
In this chapter the uncertainties of every aspect of the experimental procedure is presented. In addition, the consistency analysis will give an indication of the accurateness of the experimental procedure. This chapter is published in peer-review journals of *Fluid Phase Equilibria* and *Chemical and Engineering Data* as shown in Appendix E.

### 4.1 Calculation of hydrate equilibrium point

The uncertainties for every hydrate equilibrium point are calculated as the root of the sum of squared uncertainties of transducers and repeatability of the experimental procedure. A $P,T$ diagram is produced in order to find dissociation conditions ($T_{\text{diss}}, P_{\text{diss}}$), as it is shown for 5% TBAB and CO$_2$/N$_2$ 13.92/83.13 in Figure 4.1. The procedure is as follows. At first, the cell was cooled up to 2°C. After staying at least 10 h at this point, equilibrium is achieved which means that hydrates are fully formed. Then dissociation starts. The temperature is increased rapidly and then step-wise so that every temperature step corresponds to hydrate equilibrium dissociation point.

![Figure 4.1 Pressure-Temperature trace method diagram for estimating hydrate dissociation point. In this case for 20 wt% TBAB and CO$_2$/N$_2$ (6.87/93.13) the dissociation point is found at 32.85 bar and 12.94 °C.](image)

Figure 4.1 Pressure-Temperature trace method diagram for estimating hydrate dissociation point. In this case for 20 wt% TBAB and CO$_2$/N$_2$ (6.87/93.13) the dissociation point is found at 32.85 bar and 12.94 °C.
Finally, the dissociation point is calculated by the intersection of the VHL polynomial line with the VL equilibrium line. In this case, the dissociation point was found at 32.85 bar and 12.94 °C, according to eq. 4.1, 4.2, 4.3 and 4.4.

\[
P = a'T^2 + b'T + c'
\] for VHL equil. \hfill (4.1)

\[
P = aT + b
\] for VL equil. \hfill (4.2)

\[
T = \frac{-(b'-a)+\sqrt{\Delta}}{2\ a'} \hfill (4.3)
\]

\[
\Delta = (b' - a)^2 - 4\ a'\ (c' - b) \hfill (4.4)
\]

where

\( T \): equil. dissociation temperature

\( P \): equil. dissociation pressure

\( \Delta \): discriminant

\( a, b \): regression coefficients for VHL equil. line

\( a', b', c' \): regression coefficients for VL equil. line

\( u(a), u(b) \): regression deviations from straight line for VHL equil. line

\( u(a'), u(b'), u(c') \): regression deviations from straight line for VL equil. line

**4.2 Hydrate equipment and random uncertainties**

At first, the temperature and pressure errors \( u(T) \) and \( u(P) \) of the acquisition units were calculated. They consist of the sum of squared roots of calibration (random) and repeatability uncertainties, eq. 4.5 and 4.6. For the calibration (random) uncertainty, it is also assumed maximum error observed from the calibration polynomials, at the limits of rectangular distribution which equals to \((\sqrt{3})^{-1}\). Repeatability uncertainty entails inherently in \( P, T \) the Gaussian type distribution\(^{147}\).

\[
u(T) = \sqrt{\frac{u_{cal}^2(T)}{(\sqrt{3})^2} + u_{rep}^2(T)}
\] \hfill (4.5)
Experimental uncertainties and consistency analysis of results

Chapter 4

\[ u(P) = \sqrt{\frac{u_{\text{cal}}^2(P)}{(\sqrt{3})^2} + u_{\text{rep}}^2(P)} \]  

(4.6)

The temperature and pressure calibration error, \( u_{\text{cal}}(T), u_{\text{cal}}(P) \), was found by performing temperature and pressure measurements of liquid bath over a range of temperatures (-20 °C to 30 °C) and pressures (10 to 100 bar). The \( u_{\text{cal}}(T), u_{\text{cal}}(P) \) are found to be 0.02 K and 0.015 bar, respectively (see 3.1.1 section).

The repeatability temperature and pressure error, \( u_{\text{rep}}(T), u_{\text{rep}}(P) \) for every hydrate equilibrium point were calculated by the least square method for VHL and VL hydrate eq. dissociation points, eq. 4.7 and 4.8.

\[
\begin{align*}
\bar{u}_{\text{rep}}(T) &= \sqrt{\left[ \frac{\partial T}{\partial a} u(a) \right]^2 + \left[ \frac{\partial T}{\partial b} u(b) \right]^2 + \left[ \frac{\partial T}{\partial a'} u(a') \right]^2 + \left[ \frac{\partial T}{\partial b'} u(b') \right]^2 + \left[ \frac{\partial T}{\partial c'} u(c') \right]^2} \\
\bar{u}_{\text{rep}}(P) &= \sqrt{\left[ \frac{\partial P}{\partial a} u(a) \right]^2 + \left[ \frac{\partial P}{\partial b} u(b) \right]^2 + \left[ \frac{\partial P}{\partial a'} u(a') \right]^2 + \left[ \frac{\partial P}{\partial b'} u(b') \right]^2 + \left[ \frac{\partial P}{\partial c'} u(c') \right]^2} 
\end{align*}
\]  

(4.7)

(4.8)

Finally, the relative temperature and pressure uncertainties \( U(T) \) and \( U(P) \) are calculated using dissociation conditions, \( T_{\text{diss}} \) and \( P_{\text{diss}} \), eq. 4.9 and 4.10. A coverage factor \( k=2 \) for 95% confidence level is used assuming Gaussian distribution.

\[
\begin{align*}
U(T) &= 2 \bar{u}(T) \\
U(P) &= 2 \bar{u}(P)
\end{align*}
\]  

(4.9)

(4.10)

The results are presented in Tables B.1, B.2 and B.3 in Appendix B. The average standard uncertainty for temperature and pressure is \( U(T) \) and \( U(P) \) is 0.028 °C and 0.025 bar respectively.

4.3 Gas mixture uncertainties

Then, gas mixture errors were estimated of gas chromatograph (calibration) and repeatability \( u_{\text{cal}}(T, P, N_2), u_{\text{cal}}(T, P, CO_2) \) and \( u_{\text{rep}}(T, P, N_2), u_{\text{rep}}(T, P, CO_2) \) were calculated for every gas mixture and gas respectively. The calibration error is given by
the ratio of std. deviation of gas concentration for \(i\) number of measurements divided by the average value of gas concentration for \(i\) number of measurements. The combined uncertainty for CO\(_2\) and N\(_2\) was calculated by eq. 4.11 and 4.12.

\[
U(y_{CO_2}) = 2 \left[ \frac{u_{cal}(y_{CO_2})^2}{(\sqrt{3})^2} + \frac{u_{rep}(y_{CO_2})^2}{(\sqrt{i})^2} \right]^{1/2} \tag{4.11}
\]

\[
U(y_{N_2}) = 2 \left[ \frac{u_{cal}(y_{N_2})^2}{(\sqrt{3})^2} + \frac{u_{rep}(y_{N_2})^2}{(\sqrt{i})^2} \right]^{1/2} \tag{4.12}
\]

where \(i\): number of gas volume measurements

The \(u_{rep}(T, P)\) represents the ratio of standard deviation deviated by the root of the number for all gas measurement trials of every CO\(_2\) or N\(_2\) molar composition. In this case, denominator, \(\sqrt{n}\), is used due to the assumption of gaussian type distribution. The \(u_{cal}(T, P)\) represents the accuracy of apparatus for gas composition measurement and is shown in Table 4.1. It is also assumed maximum error observed from the calibration polynomials, at the limits of rectangular distribution which equals to \(1/\sqrt{3}\).

<table>
<thead>
<tr>
<th>Table 4.1 Gas mixtures composition uncertainties.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas mixture composition 1 (mol%)</td>
</tr>
<tr>
<td>CO(_2)</td>
</tr>
<tr>
<td>13.92</td>
</tr>
<tr>
<td>1.0%</td>
</tr>
</tbody>
</table>

In the fourth gas mixture, there is high CO\(_2\) uncertainty but the very low CO\(_2\) concentration used contribute to minimization of the absolute uncertainty. In other words, the CO\(_2\) concentration in the fourth gas mixture is 0.48±0.13 mol\%. 

62
4.4 Molar composition uncertainties

At first, CO$_2$, N$_2$, water and promoter molar masses inserted in equilibrium cell were estimated. The eq. 4.13 was used. The densities $\rho_1$ and $\rho_2$ of the inserted gas mixture was found by the pressure and temperature conditions in gas mixture cylinder with help of REFPROP software$^{148}$. The cylinder volume, $V_t$, is 0.002 m$^3$ ±0.1%.

\[
n_{\text{gas}} = V_t \left(\rho_1 - \rho_2\right) y_{\text{gas}} \frac{1}{MW_{\text{gas}}} \tag{4.13}
\]

where $n_{\text{gas}}$: mol of gas inserted in equilibrium cell

$V_t$: total cylinder volume

$\rho_1$, $\rho_2$: densities of the inserted gas mixture

$y_{\text{gas}}$: gas molar composition

$MW_{\text{gas}}$: molecular weight of gas

The gas densities $\rho_1$ and $\rho_2$ of the inserted gas mixture was found by the pressure and temperature conditions in gas mixture cylinder with help of REFPROP software$^{148}$ after each loading. The uncertainty of $n_{\text{gas}}$, $u(n_{\text{gas}})$, was estimated by eq. 4.14, 4.15 and 4.16.

\[
u(n_{\text{gas}}) = \sqrt{\left(\frac{\partial n}{\partial V_t}\right)_{V_t,P} u(V_t)^2 + \left(\frac{\partial n}{\partial \rho_1}\right)_{V_t,P} u(\rho_1)^2 + \left(\frac{\partial n}{\partial \rho_2}\right)_{V_t,P} u(\rho_2)^2} \tag{4.14}
\]

\[
u(\rho_1) = \sqrt{\left(\frac{\partial \rho_1}{\partial T}\right)_{V_t,P} u(T)^2 + \left(\frac{\partial \rho_1}{\partial P}\right)_{V_t,T} u(P)^2} \tag{4.15}
\]

\[
u(\rho_2) = \sqrt{\left(\frac{\partial \rho_2}{\partial T}\right)_{V_t,P} u(T)^2 + \left(\frac{\partial \rho_2}{\partial P}\right)_{V_t,T} u(P)^2} \tag{4.16}
\]

The $\frac{\partial \rho_1}{\partial T}$ and $\frac{\partial \rho_2}{\partial P}$ of the 1 and 2 states were estimated numerically. For estimating the gas densities $\rho_1$ and $\rho_2$, small changes of $T$, $P$ (0.01 K and 0.01 MPa respectively) allowed the estimation of gas densities using REFPROP software$^{148}$.

Finally, the standard uncertainty $U(n_{\text{gas}})$ is estimated by eq. 4.17. The water and promoter inserted quantities were estimated by the known solution volume and promoter
composition. The numerical results are shown in Table B.4 in Appendix B. The average \( U(n_{gas}) \) is 2.14%.

\[
U(n_{gas}) = 2 \frac{u(n_{gas})}{\sqrt{3} \cdot n_{gas}}
\]  

(4.17)

Other uncertainties are connected to solution and gas mixture preparation. Promoter and water weight are estimated subjectively according to experimental conditions e.g. syringe size and solute weight. The maximum water uncertainties are ±2.0 ml, for TBAF and CP ±0.1 ml respectively and the TBAB weight accuracy is ±0.01 g.

**4.5 Consistency analysis of hydrate equilibrium data**

For data treatment, Clausius–Clapeyron method is applied, eq. 4.18. Clausius-Clapeyron equation estimates the vapor pressures of liquids or solids. It is used to determine hydrate dissociation pressure as a function of heat of dissociation.

\[
\frac{d \ln(P)}{d \left( \frac{1}{T} \right)} = -\frac{\Delta H_{dis}}{Z \cdot R}
\]  

(4.18)

where \( \Delta H_{dis} \) (kJ/mmol) is the apparent dissociation enthalpy of the hydrate phase, \( Z \) is the compressibility factor and \( R \) is the gas constant. Lee-Kesler-Plöcker (LKP) Equation of State (EoS)\(^{149}\) is applied for estimation of \( Z \) as a function of \( T \) and \( P \) using binary interaction parameter \( \kappa_{ij} = 1.11 \). It is assumed very low solubility of the gas in the liquid and, thus, no changes in the gas composition.

In this study, the interest lies on the fact that for small changes of dissociation temperature, the Clausius–Clapeyron equation should predict identical (or similar) \( \Delta H_{dis} \) values. The \( \Delta H_{diss.} \) as a function of dissociation temperature shows the goodness of fit (which is shown by the Coefficient of determination \( (R^2) \)). Coefficient of determination \( (R^2) \) is used to show how well fit the \( \Delta H \) values (kJ/mol) on the straight line of \( \Delta H(T) \). Table 4.2 presents the data treatment for TBAF results of this work and from literature. The results of this work are very good \( (R^2 > 0.90) \) except for the systems of 1.38 mol% of TBAB+CP mixture. Most systems from literature are very good.
Table 4.3 presents the data treatment for CP results of this work and from literature. The results of Jianwei et al.\textsuperscript{140} and Zhang and Lee\textsuperscript{133} are not as accurate as the rest. The results from systems of CO\textsubscript{2}+TBAB+H\textsubscript{2}O and N\textsubscript{2}+TBAB+H\textsubscript{2}O from literature are presented in Table 4.4.

\textbf{Table 4.2} Coefficient of determination of $\Delta H_{\text{diss.}}$ (kJ/mol) in terms of temperature for TBAB and TBAB+CP systems of this work including TBAB literature.

<table>
<thead>
<tr>
<th>Promoter concentration (mol%)</th>
<th>CO\textsubscript{2} in CO\textsubscript{2}+N\textsubscript{2} gas mixture concentration (mol%)</th>
<th>Coefficient of determination ($R^2$)</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.29</td>
<td>6.87</td>
<td>1.000</td>
<td>this work</td>
</tr>
<tr>
<td>0.62</td>
<td>6.87</td>
<td>0.999</td>
<td>this work</td>
</tr>
<tr>
<td>1.38</td>
<td>6.87</td>
<td>0.822</td>
<td>this work</td>
</tr>
<tr>
<td>0.00</td>
<td>20.0</td>
<td>0.993</td>
<td>Olsen et al.\textsuperscript{136}</td>
</tr>
<tr>
<td>0.29</td>
<td>20.0</td>
<td>0.952</td>
<td>Meysel et al.\textsuperscript{139}</td>
</tr>
<tr>
<td>0.62</td>
<td>20.0</td>
<td>0.996</td>
<td>Meysel et al.\textsuperscript{139}</td>
</tr>
<tr>
<td>1.38</td>
<td>20.0</td>
<td>0.993</td>
<td>Meysel et al.\textsuperscript{139}</td>
</tr>
<tr>
<td>0.29</td>
<td>15.9</td>
<td>0.961</td>
<td>Lu et al.\textsuperscript{84}</td>
</tr>
<tr>
<td>1.00</td>
<td>15.9</td>
<td>0.994</td>
<td>Lu et al.\textsuperscript{84}</td>
</tr>
<tr>
<td>2.90</td>
<td>15.9</td>
<td>0.996</td>
<td>Lu et al.\textsuperscript{84}</td>
</tr>
<tr>
<td>3.70</td>
<td>15.9</td>
<td>0.998</td>
<td>Lu et al.\textsuperscript{84}</td>
</tr>
<tr>
<td>3.50</td>
<td>15.9</td>
<td>1.000</td>
<td>Lu et al.\textsuperscript{84}</td>
</tr>
<tr>
<td>0.29</td>
<td>15.0</td>
<td>0.997</td>
<td>Sfaxi et al.\textsuperscript{132}</td>
</tr>
<tr>
<td>0.55</td>
<td>15.0</td>
<td>0.996</td>
<td>Sfaxi et al.\textsuperscript{132}</td>
</tr>
<tr>
<td>0.55</td>
<td>30.0</td>
<td>0.996</td>
<td>Sfaxi et al.\textsuperscript{132}</td>
</tr>
<tr>
<td>0.29</td>
<td>15.1</td>
<td>0.608</td>
<td>Mohammadi et al.\textsuperscript{137}</td>
</tr>
<tr>
<td>0.98</td>
<td>15.1</td>
<td>0.707</td>
<td>Mohammadi et al.\textsuperscript{137}</td>
</tr>
<tr>
<td>2.34</td>
<td>15.1</td>
<td>0.812</td>
<td>Mohammadi et al.\textsuperscript{137}</td>
</tr>
<tr>
<td>0.29</td>
<td>39.9</td>
<td>0.899</td>
<td>Mohammadi et al.\textsuperscript{137}</td>
</tr>
<tr>
<td>0.98</td>
<td>39.9</td>
<td>0.972</td>
<td>Mohammadi et al.\textsuperscript{137}</td>
</tr>
<tr>
<td>2.34</td>
<td>39.9</td>
<td>0.981</td>
<td>Mohammadi et al.\textsuperscript{137}</td>
</tr>
</tbody>
</table>
The results for \( \text{CO}_2+\text{TBAB}+\text{H}_2\text{O} \) systems are very good. Almost all \( \text{N}_2+\text{TBAB}+\text{H}_2\text{O} \) systems are suspicious \((R^2<0.90)\).

### Table 4.3 Coefficient of determination of \( \Delta H_{\text{diss.}} \) in terms of temperature for systems with CP hydrates.

<table>
<thead>
<tr>
<th>CP concentration (mol%)</th>
<th>( \text{CO}_2 ) in ( \text{CO}_2+\text{N}_2 ) gas mixture concentration (mol%)</th>
<th>Coefficient of determination ((R^2))</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.03</td>
<td>6.87</td>
<td>0.983</td>
<td>this work</td>
</tr>
<tr>
<td>22.15</td>
<td>6.87</td>
<td>0.977</td>
<td>this work</td>
</tr>
<tr>
<td>16.16</td>
<td>100</td>
<td>0.980</td>
<td>Mohammadi and Richon(^{72})</td>
</tr>
<tr>
<td>17.39</td>
<td>100</td>
<td>0.886</td>
<td>Zhang and Lee(^ {133})</td>
</tr>
<tr>
<td>16.16</td>
<td>0.0</td>
<td>0.962</td>
<td>Mohammadi and Richon(^ {73})</td>
</tr>
<tr>
<td>20.42</td>
<td>0.0</td>
<td>0.975</td>
<td>Tohidi \textit{et al.}(^ {142})</td>
</tr>
<tr>
<td>5.56</td>
<td>0.0</td>
<td>0.703</td>
<td>Jianwei \textit{et al.}(^ {140})</td>
</tr>
</tbody>
</table>

### Table 4.4 Coefficient of determination of \( \Delta H_{\text{diss.}} \) in terms of temperature for \( \text{CO}_2+\text{TBAB}+\text{H}_2\text{O} \) and \( \text{N}_2+\text{TBAB}+\text{H}_2\text{O} \) systems.

<table>
<thead>
<tr>
<th>TBAB concentration (mol%)</th>
<th>( \text{CO}_2 ) in ( \text{CO}_2+\text{N}_2 ) gas mixture concentration (mol%)</th>
<th>Coefficient of determination ((R^2))</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.34</td>
<td>100</td>
<td>0.911</td>
<td>Mohammadi \textit{et al.}(^ {50})</td>
</tr>
<tr>
<td>0.69</td>
<td>100</td>
<td>0.943</td>
<td>Mohammadi \textit{et al.}(^ {50})</td>
</tr>
<tr>
<td>1.29</td>
<td>100</td>
<td>0.941</td>
<td>Mohammadi \textit{et al.}(^ {50})</td>
</tr>
<tr>
<td>2.13</td>
<td>100</td>
<td>0.992</td>
<td>Mohammadi \textit{et al.}(^ {50})</td>
</tr>
<tr>
<td>6.89</td>
<td>100</td>
<td>0.929</td>
<td>Mohammadi \textit{et al.}(^ {50})</td>
</tr>
<tr>
<td>0.29</td>
<td>100</td>
<td>0.917</td>
<td>Ye and Zhang(^ {131})</td>
</tr>
<tr>
<td>0.62</td>
<td>100</td>
<td>0.880</td>
<td>Ye and Zhang(^ {131})</td>
</tr>
<tr>
<td>1.29</td>
<td>100</td>
<td>0.882</td>
<td>Ye and Zhang(^ {131})</td>
</tr>
<tr>
<td>6.39</td>
<td>100</td>
<td>0.929</td>
<td>Ye and Zhang(^ {131})</td>
</tr>
<tr>
<td>0.29</td>
<td>0.0</td>
<td>0.759</td>
<td>Mohammadi \textit{et al.}(^ {50})</td>
</tr>
<tr>
<td>0.62</td>
<td>0.0</td>
<td>0.558</td>
<td>Mohammadi \textit{et al.}(^ {50})</td>
</tr>
<tr>
<td>1.83</td>
<td>0.0</td>
<td>0.809</td>
<td>Mohammadi \textit{et al.}(^ {50})</td>
</tr>
<tr>
<td>5.29</td>
<td>0.0</td>
<td>0.662</td>
<td>Mohammadi \textit{et al.}(^ {50})</td>
</tr>
<tr>
<td>0.29</td>
<td>0.0</td>
<td>0.624</td>
<td>Lee \textit{et al.}(^ {90})</td>
</tr>
<tr>
<td>1.38</td>
<td>0.0</td>
<td>0.773</td>
<td>Lee \textit{et al.}(^ {90})</td>
</tr>
<tr>
<td>3.59</td>
<td>0.0</td>
<td>0.725</td>
<td>Lee \textit{et al.}(^ {90})</td>
</tr>
<tr>
<td>7.73</td>
<td>0.0</td>
<td>0.893</td>
<td>Lee \textit{et al.}(^ {90})</td>
</tr>
</tbody>
</table>

Finally, the results of this work, from systems of \( \text{CO}_2+\text{TBAF}+\text{H}_2\text{O} \) and \( \text{N}_2+\text{TBAF}+\text{H}_2\text{O} \) from literature are presented in Table 4.5. The results of this work are very good \((R^2 > 0.90)\) except for the system of 0.76 mol\% of TBAF+CP mixture. The system of 0.29 mol\%
in pure CO₂ gas of Li et al.¹⁰⁴ and 1.2 mol% in pure CO₂ gas, 0.36 mol% in pure N₂ gas of Mohammadi et al.¹² as well as the systems of Lee at al.⁹⁰ are problematic ($R^2 < 0.90$). The remaining systems from the literature seem to be very good.

Table 4.5 Coefficient of determination ($R^2$) of $\Delta H_{\text{diss}}$ (kJ/mol) in terms of temperature including TBAF literature.

<table>
<thead>
<tr>
<th>Promoter concentration (mol%)</th>
<th>CO₂ global concentration of feed in CO₂+N₂ gas mixture (mol%)</th>
<th>Coefficient of determination ($R^2$)</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBAF+CP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.36</td>
<td>0.05</td>
<td>0.995</td>
<td>this work</td>
</tr>
<tr>
<td>0.76</td>
<td>0.05</td>
<td>0.864</td>
<td>this work</td>
</tr>
<tr>
<td>TBAF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.23</td>
<td>0.05</td>
<td>0.997</td>
<td>this work</td>
</tr>
<tr>
<td>0.36</td>
<td>0.05</td>
<td>0.991</td>
<td>this work</td>
</tr>
<tr>
<td>0.76</td>
<td>0.05</td>
<td>0.993</td>
<td>this work</td>
</tr>
<tr>
<td>0.29</td>
<td>100</td>
<td>0.285</td>
<td>Li et al.¹⁰⁴</td>
</tr>
<tr>
<td>0.62</td>
<td>100</td>
<td>0.984</td>
<td>Li et al.¹⁰⁴</td>
</tr>
<tr>
<td>0.14</td>
<td>100</td>
<td>0.986</td>
<td>Mohammadi et al.¹²</td>
</tr>
<tr>
<td>0.36</td>
<td>100</td>
<td>0.935</td>
<td>Mohammadi et al.¹²</td>
</tr>
<tr>
<td>1.20</td>
<td>100</td>
<td>0.734</td>
<td>Mohammadi et al.¹²</td>
</tr>
<tr>
<td>0.80</td>
<td>100</td>
<td>0.985</td>
<td>Lee at al.¹¹³</td>
</tr>
<tr>
<td>3.00</td>
<td>100</td>
<td>0.938</td>
<td>Lee at al.¹¹³</td>
</tr>
<tr>
<td>3.30</td>
<td>100</td>
<td>0.958</td>
<td>Lee at al.¹¹³</td>
</tr>
<tr>
<td>5.30</td>
<td>100</td>
<td>0.926</td>
<td>Lee at al.¹¹³</td>
</tr>
<tr>
<td>0.36</td>
<td>30.0</td>
<td>0.997</td>
<td>Sfaxi et al.¹³²</td>
</tr>
<tr>
<td>0.68</td>
<td>30.0</td>
<td>0.988</td>
<td>Sfaxi et al.¹³²</td>
</tr>
<tr>
<td>0.00</td>
<td>0.0</td>
<td>0.928</td>
<td>Van Cleeffe and Diepen¹⁴⁴</td>
</tr>
<tr>
<td>0.36</td>
<td>0.0</td>
<td>0.841</td>
<td>Mohammadi et al.¹²</td>
</tr>
<tr>
<td>1.20</td>
<td>0.0</td>
<td>0.922</td>
<td>Mohammadi et al.¹²</td>
</tr>
<tr>
<td>0.76</td>
<td>0.0</td>
<td>0.504</td>
<td>Lee et al.⁹⁰</td>
</tr>
<tr>
<td>1.69</td>
<td>0.0</td>
<td>0.627</td>
<td>Lee et al.⁹⁰</td>
</tr>
<tr>
<td>3.43</td>
<td>0.0</td>
<td>0.812</td>
<td>Lee et al.⁹⁰</td>
</tr>
<tr>
<td>5.33</td>
<td>0.0</td>
<td>0.588</td>
<td>Lee et al.⁹⁰</td>
</tr>
</tbody>
</table>

4.6 Conclusions

In this chapter experimental uncertainties and consistency analysis are presented. The temperature and pressure calibration error of transducers $u_{\text{cal.}}(T)$ and $u_{\text{cal.}}(P)$ are found to be 0.02 K and 0.015 bar, respectively. The average standard uncertainty for temperature and pressure equilibrium points $U(T)$ and $U(P)$ is 0.028 °C and 0.025 bar respectively. In addition, the standard uncertainties of gas in the four different gas mixtures are low in
absolute values. Moreover, the average standard uncertainty of gas molar composition in equilibrium cell $U(n_{\text{gas}})$ is 2.14%. Finally, the consistency analysis of every system of this work is shown in Table 4.6. The results are very satisfactory in almost all cases. Some deviations exist for mixtures of promoters but this can be attributed to the high non-ideality of their solutions. The non-ideality of promoter mixtures is due to binary gas mixture used and due to ternary aqueous solution.

Table 4.6 Coefficient of determination ($R^2$) of $\Delta H_{\text{diss.}}$ (kJ/mol) in terms of temperature for systems of this work.

<table>
<thead>
<tr>
<th>Promoter concentration (mol%)</th>
<th>CO$_2$ in CO$_2$+N$_2$ gas mixture concentration (mol%)</th>
<th>Coefficient of determination ($R^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>TBAB</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.29</td>
<td>13.92</td>
<td>0.988</td>
</tr>
<tr>
<td>0.62</td>
<td>6.87</td>
<td>0.979</td>
</tr>
<tr>
<td>0.62</td>
<td>13.92</td>
<td>0.997</td>
</tr>
<tr>
<td>1.38</td>
<td>6.87</td>
<td>0.990</td>
</tr>
<tr>
<td><strong>TBAB+CP</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.29</td>
<td>6.87</td>
<td>1.000</td>
</tr>
<tr>
<td>0.62</td>
<td>6.87</td>
<td>0.999</td>
</tr>
<tr>
<td>1.38</td>
<td>6.87</td>
<td>0.822</td>
</tr>
<tr>
<td><strong>CP</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.03</td>
<td>6.87</td>
<td>0.983</td>
</tr>
<tr>
<td>22.15</td>
<td>6.87</td>
<td>0.977</td>
</tr>
<tr>
<td><strong>TBAF</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.23</td>
<td>0.05</td>
<td>0.997</td>
</tr>
<tr>
<td>0.36</td>
<td>0.05</td>
<td>0.991</td>
</tr>
<tr>
<td>0.76</td>
<td>0.05</td>
<td>0.993</td>
</tr>
<tr>
<td><strong>TBAF+CP</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.36</td>
<td>0.05</td>
<td>0.995</td>
</tr>
<tr>
<td>0.76</td>
<td>0.05</td>
<td>0.864</td>
</tr>
</tbody>
</table>
Καθ’ ὅτι ἂν κοινωνήσωμεν ἁληθεύομεν, ὃτι ἂν ἰδιάσωμεν ψευδόμεθα.

Ἡράκλειτος ὁ Ἐφέσιος (544 – 484 π.Χ.)⁹

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⁹ *Those things we can commune with each other are real, those that we keep in privacy are fake.*

Heraclitus of Ephesus (544 – 484 BC)
5.1 Introduction

In this chapter modeling of CO$_2$+cycloalkanes (cyclopentane up to cycloctane) using van der Waals-Platteeuw (Vdw-P) hydrate model coupled with CPA EoS are discussed. The CP results of chapter 3 were modeled. This model was previously$^{20-22}$ used successfully for fluid phase - hydrate modeling. The model also predicts the hydrate structure (s(I) or s(II)). It is known that cyclopentane and cyclohexane forms s(II) structure$^{24}$ which this model predicts. For the rest cycloalkanes examined—e.g. cycloheptane, cyclooctane, methyl-cyclopentane and methyl-cyclohexane—s(H) structure is formed when these chemicals are present. Nonetheless the results are not affected by the misconception of predicting wrong hydrate structure.

5.1.1 Summary of modeling results in literature

The modeling approaches in hydrate phase equilibria modeling can be divided in three groups. The first group includes models which apply Clapeyron eq., Vdw-P model and an EoS for the fluid phases$^{112,150-157}$. The second group contains gas-gravity chart and correlations and in the third group, statistical and neural network approaches are used$^{150}$. A promising hydrate model is developed in ENSTA ParisTech in France. Paricaud$^{112}$ used SAFT-VRE model for vapor phases and electrolyte solutions together with Vdw-P model for the hydrate phase. This approach is applied satisfactorily to systems like CO$_2$+TBAB/TBAC/TBAF/TBPB+H$_2$O$^{155}$, H$_2$+TBAC+H$_2$O$^{156}$ and CO$_2$+H$_2$+TBAB/TBAF/TBPB/TBNO$_3$+H$_2$O$^{157}$.

Moreover, a research group from MINES ParisTech in France has contributed abundantly in hydrate modeling. They have used the vdw–P theory for the hydrate phase and various EoS for the fluid phases like Valderrama–Patel–Teja (VPT)$^{158}$, Peng-Robinson$^{159,160}$, non random two liquid (NRTL) activity model$^{151,159}$, Soave–Redlich–Kwong (SRK)$^{160}$, Universal Quasichemical Functional Group Activity Coefficients (UNIFAC)$^{160}$ and CPA$^{161}$ EoS. Finally, a research group from KAIST in Korea published articles 15 years ago based on SRK$^{162-165}$ and UNIFAC$^{165}$. The rest articles in literature are using various EoS.

In Table C.1 in Appendix C, literature review on hydrate modeling at the most recent
publications is presented. In Table C.2, average deviations for pressure/temperature are presented for systems from literature.

5.1.2 Paricaud’s model
The work of Paricaud\textsuperscript{112} aims at proposing a thermodynamic approach to model the SLE involving salt hydrates and gas semiclathrate hydrates. Square-well version of the SAFT-VRE (statistical associating fluid theory with variable range for electrolytes) equation of state is used. The SAFT-VRE is employed satisfactory to compute the properties of electrolyte solutions such as vapor pressures, relative apparent enthalpies, mean activity coefficients and osmotic coefficients. The advantage of electrolyte equations of state in comparison to electrolyte excess Gibbs energy models is the possibility to determine the properties of the liquid and vapor phases at high pressures with the same mathematical expression. Consequently, electrolyte equations of state require usually fewer adjustable parameters.

The SLE equilibrium conditions in electrolyte systems that involve ice and salt hydrates is combined for salt hydrates with the van de Waals-Platteeuw model\textsuperscript{19,23} for gas hydrates. Calculations are presented for HI+H\textsubscript{2}O, LiBr+H\textsubscript{2}O, and TBAB+H\textsubscript{2}O binary systems\textsuperscript{112}. In next publications the systems of CO\textsubscript{2}+TBAB/TBAC/TBAF/TBPB+H\textsubscript{2}O\textsuperscript{155}, H\textsubscript{2}+TBAC+H\textsubscript{2}O\textsuperscript{156} and CO\textsubscript{2}+H\textsubscript{2}+TBAB/TBAF/TBPB/TBNO\textsubscript{3}+H\textsubscript{2}O\textsuperscript{157} are modelled.

The results has shown excellent description of the SLE coexistence curves which can be obtained over a wide composition range by regressing two parameters $T_0$ and $\Delta h_0$ on the $T$-$x$ diagram and dissociation enthalpy data. Moreover, a very good description of the liquid-vapor-semiclathrate hydrate three-phase lines of the TBAB+CO\textsubscript{2}+H\textsubscript{2}O system is obtained. At high TBAB weight fractions, Paricaud’s model predicts a change of hydrate structure from type A to type B as pressure is increased. In addition, for initial TBAB concentrations above the stoichiometric composition, it is predicted that an increase of the initial TBAB weight fraction leads to a destabilization of the semiclathrate hydrate phase, while the opposite behavior is observed at low initial TBAB concentrations\textsuperscript{112}. 
5.2 The van der Waals-Platteeuw Hydrate Model

In this work, an approach which derives from fundamental theory of thermodynamics is applied. J. H. van der Waals and J. C. Platteeuw proposed in 1958 a hydrate model\textsuperscript{23}. This model describes only the solid hydrate phase and is typically combined with an equation of state and an activity coefficient model for the description of co-existing fluid phases. The solid phase is treated as a solid solution of hydrate formers in a crystalline host lattice.

The basic assumption in the Van der Waals-Platteeuw model concerns the chemical potential of water which at equilibrium must be equal in all phases, eq. (5.1).

\[
\mu_{w}^{\text{Hydrate}} = \mu_{w}^{\text{Liquid}} = \mu_{w}^{\text{Vapor}}
\]  

In van der Waals and Platteeuw model a meta-stable crystalline water phase is defined which preserves the same structure of water as in the actual hydrate phase, instead of evaluating absolute chemical potentials of water in the hydrate phase. This phase is called meta-stable $\beta$-phase (empty hydrate lattice).

This meta-stable phase cannot exist without the presence of guest molecules. The stabilization of the actualhydrate structure occurs due to the interaction between the guest molecule and its surrounding water molecules by van der Waals forces.

The difference in chemical potential between the actual hydrate phase and the meta-stable $\beta$-phase may be described by eq. (5.2).

\[
\mu_{w}^{\beta} - \mu_{w}^{\text{Hydrate}} = \Delta \mu_{w}^{H}
\]  

The assumptions of the guest molecule in the water cavity for the guest-host interactions were described by an approach similar to the Langmuir adsorption theory\textsuperscript{166}. The difference in chemical potential of water between a theoretical empty hydrate water lattice (empty cavities) and the actual hydrate may be described by the presence of guest molecules in the water cavities, according to monolayer Langmuir adsorption theory, eq. (5.3).
\[ \Delta \mu(T, P, \theta)_w^{\text{H}} = -R \cdot T \cdot \sum_m \left[ \nu_m \cdot \ln(1 - \sum_j \theta(T, P, \bar{y})_{m,j}) \right] \]  

(5.3)

where \( \nu_m \) is the number of cavities of type \( m \) per water molecule in the hydrate structure, \( \theta_{m,j} \) is the fractional occupancy of gas component \( j \) in cavity type \( m \). This occupancy is described by eq. (5.4):

\[ \theta(T, P, \bar{y})_{m,j} = \frac{C_{m,j} f(T, P, \bar{y})_j}{1 + \sum_j \left[ C(T)_{m,j} f(T, P, \bar{y})_j \right]} \]  

(5.4)

The fugacity \( f \) of the hydrate former is given by eq. (5.5):

\[ f(T, P, \bar{y})_j = \varphi(T, P, \bar{y})_j \cdot y_j \cdot P \]  

(5.5)

In eq. (5.4), \( C_{m,j} \) is the Langmuir constant for gas component \( j \) in cavity type \( m \), \( \varphi_j \) is the fugacity coefficient of component \( j \) in the vapor phase, \( y_j \) is the mol fraction of component \( j \) in the vapor phase. By substitution of eq. (5.4) in eq. (5.3) the following expression, eq. (5.6), for the change in chemical potential of water caused by the presence of the guest molecules is obtained.

\[ \Delta \mu(T, P, \theta)_w = R \cdot T \cdot \sum_m \left[ \nu_m \cdot \ln(1 + \sum_j \left[ C(T)_{m,j} \cdot f(T, P, \bar{y})_j \right]) \right] \]  

(5.6)

Then, it is assumed that hydrate is formed in a co-existing liquid phase. Hence, the combination of eq. (5.1) and eq. (5.2) gives eq. (5.7):

\[ \Delta \mu(T, P, \theta)_w^{\text{H}} = \mu(T, P)_{\theta}^{\text{H}} - \mu(T, P, \bar{x})_{w}^{\text{liquid}} \]  

(5.7)

At equilibrium, the chemical potential of water in the liquid phase can be described by eq. (5.8):

\[ \mu(T, P, \bar{x})_{w}^{\text{liquid}} = \mu(T, P)_{\theta} + R \cdot T \cdot \ln \left[ a(T, P, \bar{x})_{w}^{\text{liquid}} \right] \]  

(5.8)

where superscript (*) stands for a pure phase, \( a \) is the activity of water in the non-ideal liquid phase including other species. The water activity may be described either in
terms of a symmetric activity coefficient, $\gamma$, by an activity coefficient model or in terms of fugacity coefficients, $\varphi$, by an equation of state, eq. (5.9).

$$a(T, P, \theta)_w^{\text{liquid}} = \tilde{x}_w^{\text{liquid}} \cdot \gamma(T, P, \tilde{x})_w^{\text{liquid}} = \tilde{x}_w^{\text{liquid}} \cdot \frac{\varphi(T, P, \tilde{x})_w^{\text{liquid}}}{\varphi(T, P)_w}$$  \tag{5.9}$$

where $\tilde{x}_w^{\text{liquid}}$ denotes liquid phase composition of water.

Therefore, the difference in chemical potential of water between the meta-stable $\beta$-phase and water in the co-existing liquid phase is shown in eq. (5.10):

$$\Delta \mu(T, P)_w^{\text{liquid}} = \mu(T, P)_w^{\beta} - \mu(T, P)_w^{\text{liquid}} = \Delta \mu(T, P)_w^{\text{hydrate}}$$  \tag{5.10}$$

By combining the eqs. (5.6), (5.7), (5.8), (5.9) and (5.10), an explicit expression for the difference of chemical potential between the empty hydrate and the pure liquid phase at specified temperature, $T$, and pressure, $P$, is attained, eq. (5.11):

$$\Delta \mu(T, P)_w^{\text{liquid}} = R \cdot T \cdot \left\{ \sum_m [v_m \cdot \ln(1 + \sum_j (C(T)_{m,j} \cdot f(T, P, \tilde{y}_j))] + \ln \left[ \frac{\tilde{x}_w^{\text{liquid}}}{\frac{\varphi(T, P, \tilde{x})_w^{\text{liquid}}}{\varphi(T, P)_w}} \right] \right\}$$  \tag{5.11}$$

Eq. (5.11) calculates the theoretical chemical potential difference.

In this work, the fugacity and the water activity values were calculated by CPA EoS\(^{167-169}\). The last parameter to be specified is the Langmuir adsorption coefficient, $C(T)$. Van der Waals and Platteeuw\(^{23}\) suggested that the Langmuir adsorption coefficients may be estimated using Lennard-Jones-Devonshire cell theory with a Lennard-Jones 12-6 cell potential. They proposed the following expression, eq. (5.12), for the Langmuir adsorption coefficient:

$$C(T)_{m,j} = \frac{4 \cdot \pi}{k_B T} \cdot \int_0^{\infty} \exp \left( -\frac{w(r)_{m,j}}{k_B T} \right) \cdot r^2 \cdot dr$$  \tag{5.12}$$

where $k_B$ is the Boltzmann constant and $w(r)_{m,j}$ is the spherical core cell potential of component $j$ in cavity type $m$. $r$ is the linear distance from the centre of the cell. McKoy and Sinanoglu\(^{170}\) evaluated the interactions between the guest molecule and all its
surrounding first layer of water molecules and summed up the contributions in one expression for the spherical core cell potential, eq. (5.13). In 1972, Parrish and Prausnitz\textsuperscript{166}, presented the final expression for the cell potential of gas constituent $j$ in cavity type $m$, in a slightly modified form. In this work, the expression of Parrish and Prausnitz approach is utilized (eq. (5.16)).

$$w(r)_{m,j} = 2 \cdot z_m \cdot \varepsilon_j \cdot \left[ \frac{\sigma_j^{12}}{R_m^4 \cdot r} \cdot \left( \delta_{m,j}^{10} + \frac{a_j}{R_m} \cdot \delta_{m,j}^{11} \right) \right] - \frac{\sigma_j^6}{R_m^8 \cdot r} \cdot \left( \delta_{m,j}^4 + \frac{a_j}{R_m} \cdot \delta_{m,j}^5 \right) \tag{5.13}$$

Where $z_m$ is the coordination number for the guest in cavity type $m$, $\varepsilon_j$ is the characteristic energy of guest molecule $j$, $a_j$ is the core radius of molecule $j$, $\sigma_j+2 \cdot a_j$ is the collision diameter of molecule $j$, $R_m$ is the radius of cavity type $m$. $\varepsilon_j/k_B$, $a_j$ and $\sigma_j$ are called Kihara parameters. $\delta_{m,j}^N$ is defined as shown in eq. (5.14):

$$\delta_{m,j}^N = \frac{1}{N} \cdot \left[ \left( 1 - \frac{r}{R_m} - \frac{a_j}{R_m} \right)^{-N} - \left( 1 + \frac{r}{R_m} - \frac{a_j}{R_m} \right)^{-N} \right] \tag{5.14}$$

where $N$ is an integer equal to either 4, 5, 10 or 11. Kihara potential is evaluated from the cavity centre to the singularity point at $r = R_m - a_j$, Herslund\textsuperscript{20}. Thus eq. (5.12) can be rewritten as shown in eq. (5.15):

$$C(T)_{m,j} = \frac{4 \cdot \pi}{k_B T} \cdot \int_0^{R_m - a_j} \exp \left[ -\frac{w(r)_{m,j}}{k_B T} \right] \cdot r^2 \cdot dr \tag{5.15}$$

Numerical approximation of the integral in eq. (5.15) was applied by using 20 evaluation points in the Gauss-Legendre method and 200 internal sections in the Composite Simpson 3/8 rule (each with four evaluation points). The two methods produce similar results for $C(T)_{m,j}$. Due to the lower number of evaluation points, Gauss-Legendre method was applied\textsuperscript{20}. Parrish and Prausnitz\textsuperscript{166} proposed a simpler way of calculating the Langmuir adsorption coefficients\textsuperscript{171}, which is not used in this work, based on $A(T)$, $B(T)$ parameters.
In addition to the theoretical chemical potential difference, an experimental reference hydrate potential was introduced by Parrish and Prausnitz\textsuperscript{166}. The difference in chemical potential between meta-stable $\beta$-phase and pure water at specified temperature and pressure may be derived thermodynamically in terms of measurable quantities. These quantities could be determined indirectly from existing hydrate equilibrium data.

A calculation of the experimental chemical potential difference determined from a reference hydrate at reference temperature, $T_0$, and reference pressure, $P_0$, to the actual hydrate at temperature, $T$, and pressure, $P$, was done in two steps, when liquid water coexists with hydrate, according to eq. (5.17):

$$
\Delta \mu(T, P)_w^{\text{liq,Water}} = \frac{\Delta \mu(T_0, P_0)_w^{\text{liq,Water}}}{R \cdot T} - \int_{T_0}^{T} \frac{\Delta H(T, P_0)_w^{\text{ice}} + \Delta H(T)_w^{\text{liq,Water}}}{R \cdot T^2} \, dT + 
$$

$$
\int_{T_0}^{T} \frac{\Delta V_w^{\text{ice}} + \Delta V_w^{\text{liq,Water}}}{R \cdot T} \, \frac{dP_r}{dT} \, dT
$$

(5.17)

and eq. (5.18):

$$
\Delta \mu(T, P)_w^{\text{liq,Water}} = \Delta \mu(T, P_R)_w^{\text{liq,Water}} + (\Delta V_w^{\text{ice}} + \Delta V_w^{\text{liq,Water}}) \cdot (P - P_R)
$$

(5.18)

where $\Delta \mu(T, P_R)_w^{\text{liq,Water}}$ is the chemical potential difference for water at temperature, $T$ and at the dissociation pressure of the reference hydrate phase, $P_R(T)$. $\Delta \mu(T_0, P_0)_w^{\text{liq,Water}}$ is the chemical potential difference measured for the reference hydrate at reference temperature $T_0$ and reference pressure $P_0$. $\Delta H(T, P_0)_w^{\text{ice}}$ and $\Delta H(T)_w^{\text{liq,Water}}$ are the differences in molar enthalpy between ice or liquid water and empty hydrate phase respectively. $\Delta V_w^{\text{ice}}$ and $\Delta V_w^{\text{liq,Water}}$ are the differences in molar volume of between ice or liquid water and empty hydrate phase respectively. The values of reference state are determined at temperature $T_0$ and pressure, $P_0$. $P_0$ is the vapor pressure of ice at temperature, $T_0$. Since this pressure is small compared to the hydrate dissociation pressure, it is assumed zero. $T_0$ is equal to 273.15 K. $\frac{dP_r}{dT}$ is the gradient of the experimentally determined pressure-temperature curve of dissociation for the reference
hydrate phase. A three-parameter expression for the temperature dependence of the reference hydrate dissociation pressure is also presented\textsuperscript{166}.

According to assumption that the water lattice properties are independent of the guest molecule (for a given hydrate structure), the theoretical chemical potential difference provided in eq. (5.11) must be equal to the reference potential difference given by eq. (5.18) at identical temperature and pressure conditions. Hence, by equating these two expressions, and specifying either temperature or pressure, it is possible to calculate the corresponding equilibrium condition (pressure or temperature respectively).

Holder \textit{et al.}\textsuperscript{172} suggested a combined and simplified form of eqs. (5.17) and (5.18). In their expression, the use of a reference pressure, $P_R$, was removed providing a simpler expression that could be easier evaluated analytically, eq. (5.19):

$$
\frac{\Delta \mu_{(T,P)_{W}^{liq,Water}}}{R \cdot T} = \frac{\Delta \mu_{(T,P_{0})_{W}^{liq,Water}}}{R \cdot T_0} - \int_{T_0}^{T} \Delta H(T,P_{0})_{liq,Water} \cdot dT + \int_{0}^{P} \frac{\Delta V_{w}^{ice} + \Delta V_{w}^{liq,Water}}{R \cdot T} \cdot dP \quad (5.19)
$$

Holder \textit{et al.}\textsuperscript{172} argued that eq. (5.19) provides similar results compared to the before mentioned expression used by Parrish and Prausnitz\textsuperscript{158}. The version of Holder \textit{et al.}\textsuperscript{172} has also been applied successfully to more recent uses of the van der Waals-Platteeuw gas clathrate hydrate theory\textsuperscript{173,174}.

Once equilibrium conditions have been established in the model, the hydrate composition may be calculated from the fractional occupancies of the individual guests in each hydrate cavity. A water-free hydrate composition is defined according to eq. (5.20):

$$
Y_j = \sum_m \nu_m \cdot \frac{\theta^{(T,P,y)}_{m,j}}{\sum_m \nu_m \sum_l \theta^{(T,P,y)}_{m,l}} \quad (5.20)
$$

The water-free composition accounts only for the guests present in the hydrate cavities. The water lattice is ignored in the composition calculation.
5.3 Cubic-Plus-Association (CPA)

The Cubic-Plus-Association\(^{b}\) (CPA) Equation of state (EoS) is used to estimate the fugacities of all fluid phases. It was shown previously\(^{20-22}\) that CPA predicts well VLE data of CO\(_2\)+CP+H\(_2\)O hydrate system. Therefore, CPA was used in this study for higher carbon number cyclo-alkanes. CPA comprises of two contributions: a physical and association term, eq. (5.21).

\[
Z = Z_{\text{phys}} + Z_{\text{assoc}}
\]  

(5.21)

The physical term measures the deviation from ideality due to physical forces\(^{172}\). The association term consists of three groups of theories. Firstly, chemical theories are based on formation of new species and the extent of association is determined by the number of oligomers formed, as a function of density, temperature and composition\(^{172}\). Secondly, lattice theories account for the number of bonds formed between segments of different molecules that occupy adjacent sites in the lattice. The number of bonds determines the extent of association. Thirdly, in perturbation theories, the total energy of hydrogen bonding is calculated from statistical mechanics and the important parameter for hydrogen bonding is in this case the number of bonding sites per molecule\(^{172}\).

For mixtures, CPA is derived from the summation of Soave-Redlich-Kwong (SRK) EoS (phys. term) and Statistical Associating Fluid Theory (SAFT) (assoc. term)\(^{167,168}\), eq. (5.22).

\[
P = \frac{RT}{v_m-b} \left(1 - \frac{a(T)}{v_m(v_m+b)}\right) - \frac{R}{2v_m} \left(1 + \rho \frac{\partial \ln g}{\partial \rho}\right) \sum_i x_i \cdot \sum_{j \neq i} \left(1 - X_{A_{ij}} \right)
\]

(5.22)

The energy parameter \(a_i(T)\) of the EoS is given by a Soave – type temperature dependency, while \(b\) is temperature independent\(^{169}\), eq. (5.23):

\[
a_i(T) = a_{0,i} \left[1 + c_{1,i} \cdot \left(1 - \sqrt{\frac{T}{T_r}}\right)\right]^2
\]

(5.23)

\(^{b}\)Association describes the effect of hydrogen bonding upon a molecule (self–association) or upon two different molecules (cross–association) in a solution.
where \( T_r = \frac{T}{T_c,i} \) is the reduced temperature and \( c_{1,i} \) is a SRK parameter.

In the expression for the association strength \( \Delta^{AiBj} \), the parameters \( \varepsilon^{AiBj} \) and \( \beta^{AiBj} \) are called the association energy and the association volume, respectively. The key element of the association term is \( X_{Ai} \), which represents the fraction of sites \( A \) of molecule \( i \) that are not bonded with other active sites, while \( x_i \) is the mole fraction of component \( i \). \( X_{Ai} \) is related to the association strength between two sites belonging to two different molecules, e.g. site \( A \) on molecule \( i \) and site \( B \) on molecule \( j \), is determined from Kontogeorgis et al.\textsuperscript{169}, eq. (5.24):

\[
X_{Ai} = \frac{1}{1 + \rho \sum_j x_j \sum_{ij} (X_{Bj} \Delta^{AiBj})}
\]

(5.24)

where the association strength \( \Delta^{AiBj} \) in CPA is expressed in eq. (5.25) as\textsuperscript{166}:

\[
\Delta^{AiBj} = g(V_m) \left[ \exp \left( \frac{\varepsilon^{AiBj}}{kT} \right) - 1 \right] b_{ij} \cdot \beta^{AiBj}
\]

(5.25)

where \( b_{ij} = \frac{b_i + b_j}{2} \) and the radial distribution function, \( g(V_m) \) was presented in a simplified form by Kontogeorgis et al.\textsuperscript{168}. The expression for the simplified hard-sphere radial distribution function is shown in eq. (5.26).

\[
g(V_m) = \left[ 1 - \frac{1.9b}{4V_m} \right]^{-1}
\]

(5.26)

These two parameters are only used for associating components, and together with the three additional parameters of the SRK term (\( a_0, b, c_t \)), they are the five pure compound parameters of the model\textsuperscript{169}. They are obtained by fitting vapor pressure and liquid density data. For inert (not self-associating) components e.g. hydrocarbons, only the three parameters of the SRK term are required, which can be obtained either from vapor pressures and liquid densities or calculated in the conventional manner (critical data, acentric factor e.g. as done for gases like CO\(_2\) and H\(_2\)S)\textsuperscript{169}. 

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Thermodynamic modeling  Chapter 5
When CPA is used for mixtures, the conventional mixing rules are employed in the physical term (SRK) for the energy and co-volume parameters. The geometric mean rule is used for the energy parameter $a_{ij}$. The interaction parameter $k_{ij}$ is, in the applications for self-associating mixtures, e.g. alcohol, water, glycol or acid with n-alkanes, the only binary adjustable parameter of CPA\textsuperscript{169}, eq. (5.27):

$$a(T) = \sum_i \sum_j x_i \cdot x_j \cdot a_{ij}(T) \quad \text{where} \quad a_{ij}(T) = \sqrt{a_i(T) \cdot a_j(T)} \cdot (1 - k_{ij})$$

$$b = \sum_i x_i \cdot b_i$$

The interaction parameter $k_{ij}$ may be temperature-dependent, eq. (5.28):

$$k_{ij} = a_{kij} + b_{kij} \cdot T^{-1}$$

For mixtures containing two associating compounds, e.g. alcohols or glycols, combining rules for the association energy ($\varepsilon_{AiBj}$) and the association volume ($\beta_{AiBj}$) are required. The standard Combining Rule (CR-1) and the Elliott Combining Rule (ECR) have been used more successfully in previous applications\textsuperscript{20-22,168,169,175}. The expressions of the cross-association energy and cross – association volume parameters with CR-1 are shown in eq. (5.29)\textsuperscript{21}:

$$\varepsilon_{AiBj} = \frac{\varepsilon_{Ai} + \varepsilon_{Bj}}{2}, \quad \beta_{AiBj} = \sqrt{\beta_{Ai} \cdot \beta_{Bj}}$$

In CR1 the $\beta_{AiBj}$ parameter in cases of cross-association involving one non-self-associating molecule (e.g. CO$_2$+H$_2$O) is calculated directly by vapor pressure and liquid density data. For systems containing three or more components CPA becomes predictive, since only binary interactions may be accounted for (directly) in the process of parameter estimation. The methodology presented here, for handling cross-association between self-associating and non-self-association compounds corresponds to the use of the modification of the CR1 combining rule presented by Folas \textit{et al.}\textsuperscript{168}.
In this work the notation for association schemes is \([X^+;Y^-]\), where X and Y are number of sites. Superscript (+) and (-) denotes whether the sites are accepting electron (+) or donating electron (-). Water is modeled as a self-associating compound with a total of four associating sites. Two sites are electron donating (two sets of oxygen atom lone pair electrons) and two are electron accepting (two hydrogen atoms). Hence, the association scheme for water in the above defined notation becomes \([2^+;2^-]\), corresponding to the 4C association scheme as defined by Huang and Radosz\(^{176}\).

Self-association between two water molecules is modeled by allowing electron donating sites on one molecule to interact (hydrogen bond) with electron accepting sites on another molecule of the same type. The self-association strength is defined by the pure component association parameters, \(\varepsilon_{AiBj}\) and \(\beta_{AiBj}\).

### 5.4 Algorithm Applied to this work

The classical van der Waals-Platteeuw hydrate model, as presented in section 5.1, has been used with the use of computational tool of FORTRAN\(^{20}\). This section describes the numerical methods and solution procedures utilized in the model set-up as well as an overview of the overall model algorithm. The parameters required for the two models, van der Waals-Platteeuw and CPA, are found in sections 5.5.1 and 5.5.2 respectively.

This work utilizes an algorithm for the hydrate dissociation pressure calculation similar to what is presented by Parrish and Prausnitz\(^{166}\). Note that the algorithm and the hydrate model as presented above is valid only for describing equilibrium conditions for hydrate systems above the ice point temperature of water. In order to describe hydrate formation below the ice point temperature of water, the water activity correction term in eq. (5.11) must be omitted. Moreover, new reference parameters are needed for eq. (5.19).

Hydrate formation below the ice point temperature of water has not been considered in this work.

The applied procedure for hydrate dissociation pressure calculations is provided below.

1) Specify molar feeds of all components in the initial system.
2) Specify system temperature.

3) Evaluate Langmuir constants for all hydrate formers at the specified temperature of feed (for all cavities in the s(I) and s(II) hydrates).

4) Set an initial guess for pressure according to the reference pressure expressions provided by Parrish and Prausnitz\textsuperscript{166}.

5) Perform an isothermal-isobaric multi-phase flash calculation (Gibbs energy minimization) at the specified temperature and pressure, using the feed from 1).

6) Using the results from step 3) - 5), evaluate eq. (5.11)

7) Evaluate eq. (5.19) for the reference hydrate at the specified temperature and pressure.

8) Keeping compositions and fugacity coefficients constant solve eq. (5.11) and eq. (5.19) for pressure.

9) If the new pressure is different from the previously assumed, return to step 5) and repeat calculations until convergence of pressure.

The above calculation procedure is performed for both structure I and structure II hydrates. The program then chooses the most stable structure according to the criteria of lowest equilibrium pressure. Incipient hydrate equilibrium pressure, and phase composition of all phases for the specified feed and temperature is finally returned to the user. Figure 5.1 provides a graphical illustration of the calculation procedure.

The main program in the developed module concerns the van der Waals-Platteeuw hydrate model. The flash routine is used to obtain the inputs required for the hydrate model at the specified temperature and pressure.

The program solves eq. (5.11) and eq. (5.19) for the equilibrium pressure at a specific temperature. The integrals in eq. (5.19) are evaluated analytically (as presented in Herri et al.\textsuperscript{177}), eq. (5.30):

\[
\Delta \mu(T, P_R)_{\text{liq,water}} = \frac{T \cdot \Delta \mu(T_o P_o)_{\text{liq,water}}}{T_0} - \left( \Delta C_{P_0}^{\text{liq,water}} - b^{\text{liq,water}} \cdot T_0 \right) \cdot T \cdot \ln \frac{T}{T_0} - \frac{1}{2} \cdot b^{\text{liq,water}} \cdot T \cdot (T - T_0) + \left[ \Delta H(T_o, P_o)_{\text{liq,water}} - \left( \Delta C_{P_0}^{\text{liq,water}} - \right) \right]
\]
where $b_{\text{liq,water}}$ is temperature dependent coefficient of the heat capacity and $\Delta C_P^0_{\text{liq,water}}$ is molar heat capacity of reference state.

The integral of eq. (5.15) is evaluated numerically using a 20-point Gauss-Legendre quadrature method. By subtracting eq. (5.11) from eq. (5.19), the resulting equation may be solved for pressure using the 1st-order Newton-Raphson method. Keeping fugacity coefficients and fluid phase compositions constant (in van der Waals-Platteeuw model) while solving for pressure, the 1st order derivative of the function to be minimized may be approximated by eq. (5.31):
\[
\frac{df}{dp} = \Delta V_{w}^{Ice} + \Delta V_{w}^{Iq.Water} - R \cdot T \cdot \sum_j \left[ \nu_m \cdot \frac{\sum_i [c(T)_{m,i} \cdot \varphi(T, \tilde{y})_j]}{1 + \sum_i [c(T)_{m,i} \cdot \varphi(T, \tilde{y})_j]} \right] \tag{5.31}
\]

where the fugacity coefficients and fluid phase compositions are those obtained in the most recently executed flash calculation. Overall pressure convergence is obtained by successive substitution, where the pressure is substituted back and forth between the flash and the van der Waals-Platteeuw model.

### 5.5 Model Parameters

#### 5.5.1 Hydrate Model

The van der Waals-Platteeuw hydrate model parameters were found available in the literature\textsuperscript{163}. Among these are the structural parameters for the hydrate lattice. These include the average cell radii for each cavity, coordination numbers for specific cavities, number of cavities and water molecules for each hydrate unit cell etc. Such parameters are provided in Table 5.1.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Cavity</th>
<th>s(I)</th>
<th>s(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. cavities per unit cell</td>
<td>2</td>
<td>6</td>
<td>16</td>
</tr>
<tr>
<td>Avg. cavity radius·10\textsuperscript{10}/m</td>
<td>3.95</td>
<td>4.33</td>
<td>3.91</td>
</tr>
<tr>
<td>Coordination number</td>
<td>20</td>
<td>24</td>
<td>20</td>
</tr>
<tr>
<td>No. water molecules per unit cell</td>
<td>46</td>
<td>136</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.1 Water lattice and unit cell parameters for the van der Waals-Platteeuw hydrate model\textsuperscript{171}.

Other model specific parameters for the hydrate model are the thermodynamic properties of the reference hydrate. These parameters are given in Table 5.2.
Table 5.2 Thermodynamic properties for the reference hydrate in the van der Waals-Platteeuw hydrate model.

<table>
<thead>
<tr>
<th>Units</th>
<th>s(I)</th>
<th>s(II)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \mu(T_0, P_0)^{liq, Water}_w$</td>
<td>J/mol</td>
<td>1297</td>
<td>937</td>
</tr>
<tr>
<td>$\Delta H^{ice}$</td>
<td>J/mol</td>
<td>1389</td>
<td>1025</td>
</tr>
<tr>
<td>$\Delta H(T_0, P_0)^{liq, Water}_w$</td>
<td>J/mol</td>
<td>-6011</td>
<td>-6011</td>
</tr>
<tr>
<td>$\Delta C_p(T)$</td>
<td>J/(mol·K)</td>
<td>-38.12+0.141·(T-273.1)</td>
<td>-38.12+0.141·(T-273.1)</td>
</tr>
<tr>
<td>$\Delta V^{ice}_w + \Delta V^{liq, Water}_w$</td>
<td>m³/mol</td>
<td>4.6·10⁻⁶</td>
<td>4.0·10⁻⁶</td>
</tr>
</tbody>
</table>

The thermodynamic properties of the reference hydrates are determined indirectly from experimental investigations of gas hydrate systems. As these thermodynamic properties are not readily measured, the reported values often differ significantly from each other. The difficulty in comparing model results presented in literature by different authors is discussed and emphasised 177. Often an insufficient amount of information is provided about the parameters used in hydrate models. Moreover, the models are often presented in different forms, making it even more difficult to compare them.

In the present work, the thermodynamic reference properties for the hydrate structures are almost identical to those used by Sloan 174, who (at that time) successfully applied a similar version of the van der Waals-Platteeuw hydrate theory. Sloan 174, however, slightly modified the $\Delta \mu(T_0, P_0)$ for the reference hydrate.

The final parameters needed in the hydrate model are the Kihara cell potential parameters 20,24,174,179,180. Van der Waals-Platteeuw hydrate model needs a priori knowledge of the gas hydrate formers of interest. The Kihara parameters used in this work are presented in Table 5.3 and were obtained from literature. Kihara parameters for cycloalkanes and CO₂, N₂ from literature and the EoS used for their determination are presented in Appendix D, Table D.1.

Table 5.3 Kihara cell potential parameters used in this work.
Component | $a \cdot 10^{10}$ (m) | $\sigma \cdot 10^{10}$ (m) | $\varepsilon/k_B$ (K) | Reference
--- | --- | --- | --- | ---
Carbon dioxide | 0.6805 | 2.9643 | 171.70 | Herslund\textsuperscript{20}
Nitrogen | 0.3526 | 3.1723 | 128.07 | Strobel \textit{et al.}\textsuperscript{181}
Cyclopentane | 0.8968 | 3.1480 | 250.89 | Sloan\textsuperscript{174}
Methyl-Cyclopentane (mCP) | 1.0054 | 4.5420 | 353.66 | Mehta and Sloan\textsuperscript{179}
Cyclohexane (CC6) | 0.9750 | 4.2675 | 253.00 | Tohidi \textit{et al.}\textsuperscript{180}
Methyl-Cyclohexane (mCC6) | 1.0693 | 3.1931 | 407.29 | Mehta and Sloan\textsuperscript{179}
Cycloheptane (CC7) | 1.0576 | 3.5902 | 250.19 | Sloan and Koh\textsuperscript{24}
Cyclooctane (CC8) | 1.1048 | 3.6550 | 277.80 | Sloan and Koh\textsuperscript{24}

### 5.5.2 Equation of State (CPA)

The cubic-plus-association (CPA) equation of state needs three pure component parameters for non-associating compounds and five pure component parameters for self-associating compounds. Compounds that are non-self-associating, but may cross-associate with other self-associating compounds still have only three pure component parameters. In this work, carbon dioxide is treated in this way.

Pure component parameters for non-self-associating and non-cross-associating compounds are described by their critical properties in a manner identical to the Soave-Redlich-Kwong equation of state (critical temperature, critical pressure and acentric factor). The pure component parameters used in this work are provided in Table 5.4.

Water is the only component treated as self-associating in this work. Carbon dioxide can cross-associate (solvate) with water. CP, CC6, CC7, CC8, mCC6, mCCP and nitrogen are treated as non-self-associating and non-cross-associating. So, their CPA pure component parameters were calculated by their critical properties.

\textbf{Table 5.4} Cubic-Plus-Association (CPA) equation of state pure component parameters and association schemes.
Thermodynamic modeling

Compounds | Association scheme | $a_0 \cdot 10^{-5}$ | $b \cdot 10^5$ | $c_1$ | Reference
---|---|---|---|---|---
CO₂ | $[0^+;1^-]$ | 3.5079 | 2.7200 | 0.7602 | Tsivintzelis et al.\(^{182}\)
N₂ | - | 1.3820 | 2.6737 | 0.5434 | Herslund\(^{20}\)
CP | - | 1.7136 | 0.81727 | 0.7815 | Herslund\(^{20}\)
mCP | - | 2.2158 | 1.0151 | 0.8352 | This work*
CC6 | - | 2.2207 | 0.9790 | 0.8035 | This work*
mCC6 | - | 2.2158 | 1.0151 | 0.8426 | This work*
CC7 | - | 2.8067 | 1.1335 | 0.8529 | This work*
CC8 | - | 3.4740 | 1.3247 | 0.9225 | This work*
H₂O** | $[2^+;2^-]$ | 1.2277 | 1.4515 | 0.6736 | Kontogeorgis et al.\(^{183}\)

*calculated by critical properties using $a_0 = 0.427 \cdot 8.314^2 \cdot T_c/P_c$, $b = 0.08664 \cdot 8.314 \cdot T_c/P_c$, $c_1 = 0.48508 + 1.55171 \cdot \omega - 0.15613 \cdot \omega^2$ (Graboski and Daubert\(^{184}\)). The critical properties are found in CERE ThermoSystem\(^{185}\).

**For H₂O the cross association energy and volume used is 0.0692 and 1.6655 Pa·m³·mol⁻¹ respectively\(^{185}\).

All binary parameters used are presented in Table 5.5. For CO₂–H₂O, cross association volume $β_{ij}$ is found to be 0.1707\(^{20}\).

### Table 5.5 Interaction parameters ($k_{ij}$) for all binary pairs used in this work.

<table>
<thead>
<tr>
<th>Binary Pair</th>
<th>$k_{ij}$</th>
<th>Reference</th>
</tr>
</thead>
</table>
| CO₂ – H₂O | 0.4719 - 112.5 · T⁻¹ | Herslund\(^{20}\)
| CO₂ – N₂ | -0.0856 | Herslund\(^{20}\)
| CO₂ – CP | 0.1574 | Herslund\(^{20}\)
| CO₂ – CC6/CC7/CC8/mCP/mCC6 | 0.1 | Arya et al.\(^{186,\ast}\)
| N₂ – CP | 0.0 | Herslund\(^{20}\)
| H₂O – N₂ | 0.99986 - 368.4 · T⁻¹ | Herslund\(^{20}\)
| H₂O – CP | 0.0211 | Herslund\(^{20}\)

\*After personal discussion with Alay Arya, $k_{ij}$ for CO₂ – CC6/CC7/CC8/mCP/mCC6 was assumed to be 0.1.

It was also used an extension of CPA that accounts for the quadrupole moment of CO₂ which is known as qCPA\(^{187}\). The expression for the quadrupolar term is an adaptation of
the 3rd order perturbation theory developed by Stell et al.\textsuperscript{188-191}. The same base model is used like in Karakatsani et al.\textsuperscript{192,193} to develop their polar equation of state.

The following Table 5.6 summarizes the parameters used in qCPA. The association scheme in CPA for water is the same used in qCPA. CP parameters were fitted to the saturated properties.

Table 5.6 Adjusted parameters for all binary pairs used in qCPA.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$a_0 \cdot 10^{-5}$</th>
<th>$b \cdot 10^5$</th>
<th>$c1$</th>
<th>Quad. moment (q)</th>
<th>Binary Pairs</th>
<th>$k_I$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>2.9783</td>
<td>2.79</td>
<td>0.68</td>
<td>4.3</td>
<td>CO$_2$–CP</td>
<td>0.058</td>
<td>This work</td>
</tr>
<tr>
<td>CP</td>
<td>1.6296</td>
<td>7.527</td>
<td>0.7262</td>
<td>-</td>
<td>CO$_2$–H$_2$O</td>
<td>0.41-124·T$^{-1}$</td>
<td>This work</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>1.2277</td>
<td>1.451</td>
<td>0.6736</td>
<td>-</td>
<td>CP–H$_2$O</td>
<td>0.021</td>
<td>Kontogeorgis et al.\textsuperscript{183}; Herslund\textsuperscript{20}</td>
</tr>
</tbody>
</table>

### 5.6 Modeling Results

The hydrate promotion modeling results for CO$_2$+cyclo-alkane systems are presented below. The modeling results of this work are presented in Figure 5.2. In this case, feed composition data were used as calculated in this work and presented in Appendix B. The results are satisfactory.

The modeling results for CO$_2$+CC6/CC7/CC8/mCP/mCC6+H$_2$O hydrate systems are presented in Figures 5.3, 5.4, 5.5, 5.6, 5.7 and 5.8 respectively.
Figure 5.2 Hydrate dissociation points for different systems using CP as promoter and the predictive curves of vdw-P model coupled with CPA EoS for fluid phases. For clarity reasons, the systems are presented by two numbers in brackets. The first number denotes the mol fraction of CO$_2$ in N$_2$ gas mixture cylinder and the second one denotes the promoter concentration. Black markers connected with trendlines correspond to results of this work. References are presented according to their presence in figure from left to right. The upper line is produced based on feed composition data from this work. The bottom line is produced based on an assumed feed composition.

Satisfactory results are also obtained for CC7 and CC8 in Figures 5.3 and 5.4 respectively.
For CC6 the results are not so good as presented in Figure 5.5.

In the available literature\textsuperscript{180}, there was only one set of parameters available for this compound. Every Kihara parameter set in literature for every compound produce (almost) identical results. In general, the results are very much sensitive on Kihara parameters rather than CPA parameters. For mCP and mCC6, the results are not so good as shown
in Figures 5.6 and 5.7. For mCC6, above 280 K, the hydrate formation pressure increases very steeply. Similarly as with CC6, there is difficulty in modeling precisely mCC6. To match the exp. data for higher temperatures, higher $k_{ij}$ values are needed.

Finally the results for qCPA compared with CPA are shown in Fig 5.8. The two different versions of CPA are not exhibiting any differences on the results.

![Figure 5.6](image1.png)  
*Figure 5.6* Hydrate phase equilibria points and the predictive curve of the system CO$_2$+mCP+H$_2$O$^{72}$.  

![Figure 5.7](image2.png)  
*Figure 5.7* Hydrate phase equilibria points and the predictive curve of the system of CO$_2$+mCC6+H$_2$O$^{72}$.  

![Figure 5.8](image3.png)  
*Figure 5.8* Hydrate phase equilibria points and the predictive curves for CPA and qCPA EoS of the ternary system CO$_2$+CP+H$_2$O$^{72,133}$. Only for the qCPA case, the model is implemented in MATLAB by Martin Gamel Bjørner.
The average absolute deviation (AAD%) is

\[ \text{AAD\%} = \frac{1}{NP} \sum_{i=1}^{NP} \left| \frac{x_i^{\text{exp}} - x_i^{\text{cal}}}{x_i^{\text{exp}}} \right| \times 100 \]

where NP is number of data points. The average absolute error (in MPa) is the difference of predicted hydrate dissociation pressure minus the experimental pressure.

The following Table 5.7 summarises the AAD% for every hydrate system.

<table>
<thead>
<tr>
<th>System</th>
<th>AAD%</th>
<th>References of experimental data</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂+N₂+CP(6.03 mol%)+H₂O</td>
<td>9.1</td>
<td>This work</td>
</tr>
<tr>
<td>CO₂+N₂+CP(22.15 mol%)+H₂O</td>
<td>8.2</td>
<td>This work</td>
</tr>
<tr>
<td>CO₂+CP+H₂O</td>
<td>8.0</td>
<td>Mohammadi and Richon\textsuperscript{72}</td>
</tr>
<tr>
<td>CO₂+CC₆+H₂O</td>
<td>21.1</td>
<td>Mohammadi and Richon\textsuperscript{72}</td>
</tr>
<tr>
<td>CO₂+CC₇+H₂O</td>
<td>0.0</td>
<td>Mohammadi and Richon\textsuperscript{194}</td>
</tr>
<tr>
<td>CO₂+CC₈+H₂O</td>
<td>2.2</td>
<td>Mohammadi and Richon\textsuperscript{194}</td>
</tr>
<tr>
<td>CO₂+mCP+H₂O</td>
<td>2.9</td>
<td>Mohammadi and Richon\textsuperscript{72}</td>
</tr>
<tr>
<td>CO₂+mCC₆+H₂O</td>
<td>9.8</td>
<td>Mohammadi and Richon\textsuperscript{72}</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>8.9</strong></td>
<td></td>
</tr>
</tbody>
</table>

### 5.7 Conclusions - Looking ahead on Modeling of TBA salts

This chapter presented predictive results of CP systems of this work and for systems of CO₂+cycloalkane+H₂O hydrates. The results are satisfactory in almost all cases even though the Kihara parameters used were excerpted from literature while various EoS were used for their estimation in many of the cases. Only cyclohexane results are not perfectly matching the experimental data and this is caused by the modified VPT with non-density-dependent mixing rules EoS used for the Kihara parameters as shown in Table D.1.

The model used in this work should be extended to deal with TBA salts. This is not straightforward because TBA salts form semi-clathrate hydrates which require, apart from new CPA and Kihara parameters, new thermodynamic parameters (Tables 5.2-5.4). More specifically, there are many structural studies\textsuperscript{13,28,112,113,115,118,145,146,152} for water lattice and unit cell parameters for semi-clathrates (as presented in Table 5.1).
Experiments should be carried out in order to find the chemical potential and enthalpies\textsuperscript{112} of water lattice and ice for semi-clathrate structures at standard conditions (as presented in Table 5.2). Then, new Kihara parameters (as presented in Table 5.3) could be calculated with this model. CPA could then calculate CO\textsubscript{2} and N\textsubscript{2} solubility in TBAB aqueous solution. Finally, coupled with CPA parameters, this model could then predict TBAB and TBAF results. Fugacities will be more difficult to calculate since TBA salts dissociate in aqueous solution.
Ἐφ᾿ ὅσον χρόνον τίς ἔστιν ἐν τῇ ζωῇ ταύτῃ, κἂν τέλειος ἔστι κατὰ τὴν ἐνθάδε κατάστασιν, καὶ πράξει καὶ θεωρίᾳ, τὴν ἐκ μέρους ἔχει καὶ γνῶσιν καὶ προφητείαν καὶ ἀῤῥαβώνα Πνεύματος ἁγίου· ἀλλ᾿ οὐκ αὐτὸ τὸ πλήρωμα· ἔλευσόμενος ποτε μετὰ τὴν τῶν αἰώνων περαίωσιν εἰς τὴν τελείαν λῆξιν, τὴν πρόσωπον πρὸς πρόσωπον τοῖς ἀξίοις δεικνύσαν αὐτὴν ἐφ᾿ ἑαυτῆς ἑστῶσαν τὴν ἀλήθειαν· ὡς μηκέτι ἐκ τοῦ πληρώματος μέρος ἔχειν, ἀλλ᾿ αὐτὸ τὸ πλήρωμα τῆς χάριτος κατὰ μέθεξιν ὅλον κομίζεσθαι.

Ἀγ. Μάξιμος ὁ Ὀμολογητής (580 – 662 μ.Χ.)

\[1\] As long as somebody exists in this life, even if he is perfect in this (earthy) situation, concerning action and theory, he has partly knowledge and prophesy and engagement of Holy Spirit’ but this (is) not the fulfillment/all when (he) comes at some point after the ending of centuries in the perfect expiration, face to face to the worthy (people), it will appear the self-sustained Truth’ so as he may not have any more part of the fulfillment/all, but (he will) acquire all this fulfillment of Grace through communion.

St. Maximus the Confessor (580 – 662 AD)
6.1 Conclusions

The PhD Thesis dealt with the production of hydrate equilibrium data of TBA salts and cyclopentane and modeling of cycloalkane hydrates. Gas hydrate crystallization can be used as a post-combustion capture process\(^7\). The scope of this method is to capture CO\(_2\) from flue gas by the mean of hydrates and then its release so that CO\(_2\) is purely concentrated in one stream. This technology is immature, requires high pressure for the hydrates to form and it exhibits large energy penalty\(^{51}\). High pressure is linked with high operational costs\(^9,10\) (chapters 1 and 2). Therefore, the use of chemicals (promoters) to produce hydrates at lower pressures is imperative. The available literature review (of chapter 2) showed that there is shortage in data of CO\(_2\)+N\(_2\) gas mixture which is a common effluent in oil and gas industry\(^10\). Moreover, TBAF promoter, which has high capability in reducing hydrate equilibrium pressure, has not been examined as extensively as THF. Hydrate equilibrium points for CO\(_2\) and N\(_2\) were measured with the use of tetra-n-butyl ammonium bromide (TBAB), tetra-n-butylammonium bromide (TBAF), cyclopentane (CP) and mixtures of TBAB and TBAF with CP as promoters (chapter 3). The use of higher TBAB concentration (1.38 mol\%) and CP (5 vol\%) revealed promotion effect and as the pressure increases (>3.5 MPa), the promotion effect increases. In addition, the higher the CO\(_2\) concentration, the stronger the promotion is for every TBAB solution which is shown by the shift of equilibrium points at higher temperatures. On the contrary, the results have shown that the simultaneous use of TBAB (0.29 mol\%) and (0.62 mol\%) with CP (5 vol\%) did not have any impact on thermodynamic equilibrium. For the system TBAB (0.29 mol\%) with CP (5 vol\%), even though the gas mixture systems are different, it is rather unlikely that there is positive impact in promotion. However, this fact is not easily observable for low differences of CO\(_2\) concentration in gas mixtures with N\(_2\). Consequently, it came out that the factor of gas mixture concentration has moderate impact on hydrate equilibrium points compared to promoter’s concentration. The results of this work are presented in Figure 3.18.

The use of CP solution (even though it is virtually water inmiscible) proved to be stronger promoter than TBAB maybe because of the different hydrate structure it induces. The CP
drawback, however, is the low CO₂ selectivity in gas hydrate in CO₂ + N₂ gas mixture. The stoichiometric concentration of CP in the solution for structure II hydrates is 18.65 wt% (5.56 mol%). When higher CP concentration than this value was used, e.g. 52 wt% (22.15 mol%), the results showed slight inhibition effect. Finally, the data consistency analysis carried out using Clausius-Clapeyron method revealed that the measurements of this work are satisfactory.

Hydrate equilibrium points for CO₂ and N₂ were measured with the use of tetra-n-butylammonium bromide (TBAF) and mixture of TBAF with CP as promoters. The use of TBAF concentration (0.36 mol%) and CP (5 vol%) revealed a promotion effect at pressures higher than 3.5 MPa. On the contrary, the results have shown that the simultaneous use of TBAF (0.76 mol%) with CP (5 vol%) did not have any impact on thermodynamic equilibrium. The equilibrium results are more dependent on TBAF concentration rather than gas mixture concentration as the comparison with literature data revealed. The consistency analysis has shown that the results of this study are satisfactory.

In addition, experimental uncertainties and consistency analysis are calculated and presented (chapter 3 and 4). The temperature and pressure calibration uncertainties of transducers $u_{\text{cal}}(T)$ and $u_{\text{cal}}(P)$ are found to be 0.02 K and 0.015 bar, respectively. The average standard uncertainty for temperature and pressure equilibrium points are $U(T)$ and $U(P)$ is 0.028 °C and 0.025 bar respectively. In addition, the standard uncertainties of gas in the four different gas mixtures are low in absolute values. Moreover, the average standard uncertainty of gas molar composition in equilibrium cell $U(n_{\text{gas}})$ is 2.14%. The consistency analysis of every system of this work (chapter 4) is shown in Table 4.6. The results are very satisfactory in almost all cases. Some deviations exist for mixtures of promoters. This can be attributed to the high non-ideality of their solutions which Clapeyron equation is not applicable.

Finally, the van der Waals-Platteeuw hydrate model was used for modeling the CP results of this work and for cycloalkanes of higher carbon number (chapter 5). The predictive results of CP systems of this work (Figure 5.2) and for systems of
CO$_2$+cycloalkane+H$_2$O hydrates are very satisfactory in almost all cases even though the Kihara parameters used were excerpted from literature while various EoS were used for their estimation in many of the cases. Cyclohexane results are not perfectly matching the experimental data. This is due to the modified PVT with non-density-dependent mixing rules EoS which is used for the estimation of Kihara parameters as shown in Table D.1. Modified PVT is intrinsically different than CPA EoS.

### 6.2 Future steps to technological scale-up

#### 6.2.1 Process design aspects

The comparison of CO$_2$ capture technologies against CO$_2$ hydrate crystallization has shown that hydrate crystallization can be competitive under three conditions:

- a) CO$_2$-rich feed phase
- b) High pressure inlet gas such as in oil and gas industry
- c) Consideration of crystallization as long-term capturing technology

In Figure 6.1, a comparison of different CO$_2$ capture technologies is presented. It is shown that hydrate technology has comparable cost to other technologies in the iron and steel production where the CO$_2$ concentration to be treated is typically 30-50 mol%.

The process design of a crystallization unit is generally simple. However, the design issues in hydrate crystallization to be considered are:

- a) operating temperature
- b) minimum pressure
- c) rate of hydrate growth
- d) gas uptake (separation efficiency).
Figure 6.1 CO₂ avoidance costs and avoidance rates for iron and steel production in the short-mid term future (10-15 years) and the long term future (20 years or more). The error bars present uncertainty ranges. The dotted lines indicate the probable future CO₂ price range (30-75 Euro/t)\(^{10}\).

In this study, the focus was only on pressure reduction. However, the issues (c) and (d) are also crucial. In Figure 6.2, CO₂ uptake is presented for every hydrate structure. The maximum CO₂ uptake can be achieved from s(I) or s(II) hydrate (without promoter). But CO₂ alone cannot stabilize the s(II) hydrates\(^{24}\). Promoters like THF, CP or propane occupy some of the large cages of the s(II) hydrate and reduces the CO₂ uptake considerably. Similarly, in case of TBAB semi-clathrate hydrates, only small cages are available for CO₂ and hence a lower CO₂ uptake capacity.
Figure 6.2 CO$_2$ gas uptake for every gas hydrate structure$^{196}$.

Several reactor configurations have been proposed in the literature$^{78-110}$. Most of the studies were carried out in a laboratory scale continuous stirring tank reactor (CSTR). CSTRs are currently used to investigate kinetics of hydrate formation and phase equilibrium measurements. The CSTR has certain disadvantages such as low water conversion to hydrate, gas uptake, slow kinetics and significant energy penalty for stirring. Low water conversion to hydrate is not desirable for scaling up the hydrate crystallisation process for CO$_2$ capture$^{196}$.

Among the various reactor configurations employed so far, fluidized bed reactor (FBR) configuration can be potentially applied at a commercial scale. The drawback of FBR is the requirement of immiscible promoter. The advantages of FBR are the increased gas-liquid contact area; enhanced kinetics and the energy save due to lack of stirring. Moreover, Polyurethane foam or silica sand are cheap and readily available compared to silica gel$^{60,126,127,199,200}$ and other porous medium tested until now.

In Figure 6.3, it is to observe the normalised rate of hydrate growth and gas uptake against various promoters for different reactor configurations. The outcome is that propane exhibit the highest CO$_2$ gas uptake from the until now (2015) available data even though there are relative high fluctuations of the values for same $P,T$ conditions and promoter concentrations.
There are also other processes proposed in the literature. A continuous reactor was proposed in the \textit{SMTECHE process}\textsuperscript{201}. The \textit{SIMTECHE process} takes advantage of the higher pressure of the pre-combustion streams in an IGCC power plant to remove CO\textsubscript{2} by clathrate hydrate formation. The major limitation of employing continuous mode for the hydrate crystallisation process is the possible plug which is caused by hydrate formation and can block the pipelines e.g. the oil and gas flow lines. The other drawbacks of the continuous operation of the hydrate crystallisation process are insufficient residence time to achieve higher water conversions and higher operating costs involved in gas/liquid agitation for hydrate formation\textsuperscript{196}.
Moreover, hydrate technology design coupled with membranes for post-combustion capture was presented in 2007 in Figure 6.4. It is the most recent design in literature concerning post-combustion carbon capture. However, there are more recent available designs for pre-combustion carbon capture\textsuperscript{190,191}.

It is evident from the brief discussion of the hydrate issues of hydrate technology that more work needs to be done both on technological specifications and scale-up.

![Figure 6.4 A hybrid hydrate-membrane process for CO\textsubscript{2} recovery from flue gas\textsuperscript{7}.](image)

**6.2.2 Future work**

It is profound from the existing literature so far that the field of hydrate promotion is lacking in both experimental results and modeling work. The research should focus on examination of new chemicals and combination of them as it was shown in this study as well as to kinetic and structural studies to get a better understanding of their actual capabilities. Techniques with higher efficiency and cost effectiveness are essential but the scale-up challenges of novel technologies from a laboratory to industrial scale has also to be addressed to manage effectively the technical difficulties in CCS.

Apart from testing new components for finding a potential promoter, modeling work should need to provide the necessary aid to this target. The attempts so far are not utterly convincing\textsuperscript{198} but, nevertheless, it can be considered as a start: *the beginning is half of...*
everything as philosopher Pythagoras stated. In addition, the model used in this work should be extended to deal with TBA salts. This is not straightforward because TBA salts form semi-clathrate hydrates which require, apart from new CPA and Kihara parameters, new thermodynamic parameters (Tables 5.2-5.4). More specifically, there are many structural studies\textsuperscript{13,28,112,113,115,118,145,146,150} for water lattice and unit cell parameters for semi-clathrates (as presented in Table 5.1). There should be experiments to find the chemical potential and enthalpies\textsuperscript{112} of water lattice and ice for semi-clathrate structures at standard conditions (as presented in Table 5.2). Then, new Kihara parameters (as presented in Table 5.3) could be calculated with this model. CPA could then calculate CO\textsubscript{2} and N\textsubscript{2} solubility in TBAB aqueous solution. Finally, coupled with CPA parameters, this model could then predict TBAB and TBAF results. Fugacities will be more difficult to calculate since TBA salts dissociate in aqueous solution.

In general, pre-combustion (for high pressure, mainly CO\textsubscript{2}/H\textsubscript{2} separation), post-combustion (low pressure, mainly CO\textsubscript{2}/N\textsubscript{2}), and oxy-fuel combustion (predominantly CO\textsubscript{2}/H\textsubscript{2}O separation) techniques along with new promoters and processes can provide a solution to solve the CO\textsubscript{2} capture and separation (CCS) challenge. To cope with this convoluted issue, multiple technologies would need to be integrated\textsuperscript{107}. 


Bibliography


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Bibliography


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Appendix A

The next Tables A.1 and A.2 present CO₂ hydrate experiments without and with promoter, respectively.

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<td>Uchida *et al.*⁴³</td>
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occupied by hydrogen molecules

Seo and Kang\textsuperscript{209} CO\textsubscript{2} + H\textsubscript{2} 274.15 6.0– 9.2 PVT studies on dissociation conditions + \textsuperscript{13}C NMR on cage occupancy by hydrogen molecules in hydrate formed in silica gel particles

Sugahara \textit{et al.}\textsuperscript{210} CO\textsubscript{2} + H\textsubscript{2} 274.3– 281.9 1.42– 9.13 Raman spectroscopy using quartz windows on cage occupancy by hydrogen molecules and direct gas release method

Ma \textit{et al.}\textsuperscript{211} CO\textsubscript{2} + H\textsubscript{2}, CO\textsubscript{2} + H\textsubscript{2} + N\textsubscript{2}, CO\textsubscript{2} + H\textsubscript{2} + CH\textsubscript{4}, CO\textsubscript{2} + CH\textsubscript{4} + C\textsubscript{2}H\textsubscript{4} 277.7– 288.2 0.28– 2.05 PVT studies on equilibrium conditions of semi-clathrate hydrate

Surovtseva \textit{et al.}\textsuperscript{212} CO\textsubscript{2} + H\textsubscript{2} + N\textsubscript{2} + CH\textsubscript{4} + Ar + para-toluene sulphonate acid (PTSA) 222 2.8, 5.3, 5.7 Combination of a gas hydrate formation process with a low temperature cryogenic one for capturing CO\textsubscript{2} from a coal gas stream. The operational conditions and the amount of captured CO\textsubscript{2} have been reported.

**Table A.2** Experimental studies on clathrate/semi-clathrate hydrate for CO\textsubscript{2} + gas/gases systems + H\textsubscript{2}O + promoters.

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### Appendices

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<td>PVT and kinetic studies on hydrate formation conditions, gas consumption, induction time of semi-clathrate gas hydrates of a flue gas containing (\text{CO}_2 + \text{H}_2) in a hydrate formation reactor. Enclathration of (\text{CO}_2) molecules observed by Raman Spectroscopy</td>
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\(^{116}\) Fan et al., \(^{57}\) Kim et al., \(^{102}\) Li et al., \(^{70}\) Li et al., \(^{118}\) Lin et al.
differential thermal analysis (DTA) under pressure

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PVT studies on dissociation conditions of gas hydrates

PVT studies on equilibrium conditions of semi-clathrate hydrate in a jacketed isochoric cell reactor
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<td>Park et al.</td>
<td>( \text{CO}_2 + \text{H}_2 + \text{TBAB} ), ( \text{CO}_2 + \text{H}_2 + \text{TBAF} )</td>
<td>282–290, 293–302</td>
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<td>Xia et al.</td>
<td>( \text{CO}_2 + \text{CH}_4 + \text{TBAB} ), ( \text{CO}_2 + \text{CH}_4 + \text{THF} ), ( \text{CO}_2 + \text{CH}_4 + \text{Dimethyl sulfoxide (DMSO)} ), ( \text{CO}_2 + \text{CH}_4 + \text{TBAB} + \text{DMSO} ), ( \text{CO}_2 + \text{CH}_4 + \text{THF} + \text{DMSO} )</td>
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<td>0.19–2.52</td>
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<tr>
<td>Hashimoto et al.94</td>
<td>$\text{CO}_2 + \text{H}_2 + \text{THF}$</td>
<td>280.1</td>
<td>0.23–2.46</td>
<td>PVT studies, Raman spectroscopy</td>
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<td>Herslund et al.22</td>
<td>$\text{CO}_2 + \text{THF}$</td>
<td>283.3–285.2</td>
<td>0.61–0.91</td>
<td>PVT and kinetic studies on hydrate formation conditions, water consumption + compositions of promoters in equilibrium with gas hydrate</td>
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<td>Kang and Lee95</td>
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<td>272–295</td>
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<td>Lee et al.85</td>
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<td>Lee et al.111</td>
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<td>PVT studies, gas and hydrate phase composition, Raman and XRD spectroscopy</td>
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<td>$\text{CO}_2 + \text{CH}_4 + \text{THF}$</td>
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<td></td>
<td></td>
<td>290</td>
<td>1.37–2.36</td>
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<td>Linga et al.83</td>
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<td>1.5</td>
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<tr>
<td>Martinez et al.86</td>
<td>$\text{CO}_2 + \text{THF}$</td>
<td>275–303</td>
<td>0.21–2.01</td>
<td>Measurements of dissociation enthalpy via</td>
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### Appendices

<table>
<thead>
<tr>
<th>Authors</th>
<th>System</th>
<th>Temperature Range</th>
<th>PVT Studies</th>
<th>Complementary Studies</th>
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<td>Sabil et al.</td>
<td>$\text{CO}_2 + \text{THF}$</td>
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<td>PVT studies, dissociation enthalpy, compressibility factor</td>
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<td>Sabil et al.</td>
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<td>Sabil et al.</td>
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<td>1.73–2.03</td>
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<td>Yang et al.</td>
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<td>3.00–8.23</td>
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<td>Makino et al.</td>
<td>$\text{CO}_2 + \text{TBAC}$</td>
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<td>Mayoufi et al.</td>
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127
## Appendices

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<th>System</th>
<th>Pressure Range (MPa)</th>
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<th>Dissociation Enthalpy (kJ/mol)</th>
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<td>$\text{CO}_2 + \text{tetrahydropyran (THP)}$</td>
<td>280.43--291.47</td>
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<td>$\text{CO}_2 + \text{cyclobutanone (CB)}$</td>
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Zhang and Lee\textsuperscript{133}

<table>
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<th>Temperature Range (°C)</th>
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<td>2.60--3.66</td>
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</table>

Li et al.\textsuperscript{71}

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<th>Temperature Range (°C)</th>
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<td>3.5--15</td>
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Zhang et al.\textsuperscript{88}

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<tr>
<td>$\text{CO}_2 + \text{3-methyl-1-butanol (3M1B)}$</td>
<td>272.6--282.8</td>
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Shin et al.\textsuperscript{92}

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<th>Dissociation Enthalpy (kJ/mol)</th>
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<td>1.08--2.76</td>
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<td>$\text{CO}_2 + \text{acetone}$</td>
<td>270.05--279.15</td>
<td>0.81--2.54</td>
<td></td>
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<tr>
<td>$\text{CO}_2 + \text{DXN}$</td>
<td>274.65--280.95</td>
<td>1.08--2.76</td>
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Seo et al.\textsuperscript{79}

The kinetics of hydrate formation in a flue gas sample containing $\text{CO}_2 + \text{N}_2$ have been studied in a reactor along with measurements of vapor and hydrate compositions at equilibrium.

Seo et al.\textsuperscript{79}

Measurements of dissociation enthalpy via DSC under pressure.

Seo et al.\textsuperscript{79}

PVT studies, Raman spectroscopy, XRD.

Seo et al.\textsuperscript{79}

PVT studies.
Appendices

Shin et al.92

\[ \text{CO}_2 + \text{acetone} \quad 270.05 - 279.15 \quad 0.81 - 2.54 \]

Van Denderen et al.93

\[ \begin{align*}
\text{CO}_2 + \text{CH}_4 + \text{THF} & \quad 275.15 \quad 1.5 - 8 \\
\text{CO}_2 + \text{CH}_4 + \text{Cetyl trimethyl ammonium bromide (CTAB)} & \quad 275.15 \quad 6 - 8 \\
\text{CO}_2 + \text{CH}_4 + \text{fluorosurfactant} & \quad 275.15 \quad 6 - 8 \\
\end{align*} \]

Servio et al.224

\[ \text{CO}_2 + \text{CH}_4 + \text{neohexane} \quad 273.9 - 283.2 \quad 1.3 - 5.10 \]

PVT studies, Raman spectroscopy, XRD, Kinetic studies

Appendix B

Experimental uncertainties of temperature and pressure are shown in Tables B.1, B.2, and B.3.

Table B.1 Hydrate equilibrium points for CP and TBAB+CP solutions with temperature and pressure uncertainties.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Pressure</th>
<th>CP</th>
<th>CO(_2) in CO(_2) +(\text{N}_2) gas mixture</th>
<th>U(T)</th>
<th>U(P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>°C</td>
<td>bar</td>
<td>MPa</td>
<td>wt% (mol%)</td>
<td>mol%</td>
</tr>
<tr>
<td>286.73</td>
<td>13.58</td>
<td>19.97</td>
<td>2.00</td>
<td>20 (6.03)</td>
<td>6.87</td>
</tr>
<tr>
<td>286.41</td>
<td>13.26</td>
<td>18.91</td>
<td>1.89</td>
<td>(22.15)</td>
<td>52.57</td>
</tr>
<tr>
<td>289.27</td>
<td>16.12</td>
<td>34.54</td>
<td>3.45</td>
<td>(22.15)</td>
<td>52.57</td>
</tr>
<tr>
<td>293.04</td>
<td>19.89</td>
<td>65.09</td>
<td>6.51</td>
<td>(22.15)</td>
<td>52.57</td>
</tr>
</tbody>
</table>

TBAB - wt% (mol%) + CP (5 vol%)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Pressure</th>
<th>CP</th>
<th>CO(_2) in CO(_2) +(\text{N}_2) gas mixture</th>
<th>U(T)</th>
<th>U(P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>°C</td>
<td>bar</td>
<td>MPa</td>
<td>wt% (mol%)</td>
<td>mol%</td>
</tr>
<tr>
<td>280.20</td>
<td>7.05</td>
<td>22.10</td>
<td>2.21</td>
<td>5 (0.29)</td>
<td>6.87</td>
</tr>
<tr>
<td>281.45</td>
<td>8.30</td>
<td>32.66</td>
<td>3.27</td>
<td>5 (0.29)</td>
<td>6.87</td>
</tr>
<tr>
<td>282.82</td>
<td>9.67</td>
<td>49.64</td>
<td>4.96</td>
<td>5 (0.29)</td>
<td>6.87</td>
</tr>
<tr>
<td>283.59</td>
<td>10.44</td>
<td>62.16</td>
<td>6.22</td>
<td>5 (0.29)</td>
<td>6.87</td>
</tr>
<tr>
<td>282.75</td>
<td>9.60</td>
<td>19.51</td>
<td>1.95</td>
<td>10 (0.62)</td>
<td>6.87</td>
</tr>
<tr>
<td>284.25</td>
<td>11.10</td>
<td>33.76</td>
<td>3.38</td>
<td>10 (0.62)</td>
<td>6.87</td>
</tr>
<tr>
<td>285.41</td>
<td>12.26</td>
<td>49.35</td>
<td>4.94</td>
<td>10 (0.62)</td>
<td>6.87</td>
</tr>
<tr>
<td>286.34</td>
<td>13.19</td>
<td>65.50</td>
<td>6.55</td>
<td>10 (0.62)</td>
<td>6.87</td>
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<tr>
<td>285.38</td>
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<td>1.86</td>
<td>20 (1.38)</td>
<td>6.87</td>
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Table B.2 Hydrate equilibrium points for TBAB solution with temperature and pressure uncertainties.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Pressure</th>
<th>TBAB</th>
<th>CO₂ in CO₂ +N₂ gas mixture</th>
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<tbody>
<tr>
<td>K</td>
<td>ºC</td>
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<td>MPa</td>
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<tr>
<td>279.83</td>
<td>6.68</td>
<td>18.26</td>
<td>1.83</td>
</tr>
<tr>
<td>281.47</td>
<td>8.32</td>
<td>37.68</td>
<td>3.77</td>
</tr>
<tr>
<td>281.48</td>
<td>8.33</td>
<td>23.07</td>
<td>2.31</td>
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<tr>
<td>283.15</td>
<td>10.00</td>
<td>42.13</td>
<td>4.21</td>
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<tr>
<td>284.21</td>
<td>11.06</td>
<td>52.98</td>
<td>5.30</td>
</tr>
<tr>
<td>284.74</td>
<td>11.59</td>
<td>62.14</td>
<td>6.21</td>
</tr>
<tr>
<td>285.01</td>
<td>9.36</td>
<td>18.87</td>
<td>1.89</td>
</tr>
<tr>
<td>284.3</td>
<td>11.15</td>
<td>34.23</td>
<td>3.42</td>
</tr>
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<td>285.17</td>
<td>12.02</td>
<td>48.44</td>
<td>4.84</td>
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<td>286.56</td>
<td>13.41</td>
<td>64.47</td>
<td>6.45</td>
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<tr>
<td>283.83</td>
<td>10.68</td>
<td>23.06</td>
<td>2.31</td>
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<tr>
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<td>3.61</td>
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<tr>
<td>286.91</td>
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<td>53.76</td>
<td>5.38</td>
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<td>14.03</td>
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<td>288.04</td>
<td>14.89</td>
<td>61.58</td>
<td>6.16</td>
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Table B.3 Hydrate equilibrium points for TBAF solution with temperature and pressure uncertainties.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Pressure</th>
<th>TBAF</th>
<th>CO₂ in CO₂ +N₂ gas mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>ºC</td>
<td>bar</td>
<td>MPa</td>
</tr>
<tr>
<td>293.18</td>
<td>20.03</td>
<td>20.32</td>
<td>2.03</td>
</tr>
<tr>
<td>293.61</td>
<td>20.46</td>
<td>35.50</td>
<td>3.55</td>
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<tr>
<td>293.91</td>
<td>20.76</td>
<td>50.13</td>
<td>5.01</td>
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<tr>
<td>294.14</td>
<td>20.99</td>
<td>64.17</td>
<td>6.42</td>
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<td>79.13</td>
<td>7.91</td>
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<tr>
<td>287.05</td>
<td>13.90</td>
<td>9.68</td>
<td>0.97</td>
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Molar concentration uncertainties of inserted gas are shown in Tables B.4.

Table B.4 Gas molar composition and gas inserted uncertainty $U(n_{\text{gas}})$ for every hydrate equilibrium point.

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<th>CO$_2$ inserted (mol)</th>
<th>N$_2$ inserted (mol)</th>
<th>H$_2$O inserted (mol)</th>
<th>Promoter inserted (mol)</th>
<th>U($n_{\text{gas}}$)</th>
<th>CO$_2$ in CO$_2$ + N$_2$ gas mixture (mol%)</th>
<th>Promoter concentration (wt%)</th>
</tr>
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<tbody>
<tr>
<td>0.00773</td>
<td>0.0692</td>
<td>1.31</td>
<td>0.00403</td>
<td>1.89%</td>
<td>14.92%</td>
<td>5% TBAB</td>
</tr>
<tr>
<td>0.00698</td>
<td>0.0626</td>
<td>1.31</td>
<td>0.00403</td>
<td>2.02%</td>
<td>14.92%</td>
<td>5% TBAB</td>
</tr>
<tr>
<td>0.01673</td>
<td>0.1499</td>
<td>1.31</td>
<td>0.00403</td>
<td>1.75%</td>
<td>14.92%</td>
<td>5% TBAB</td>
</tr>
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Appendix C

The Table C.1 summarises recent works in hydrate phase equilibria modeling. The systems examined for many of these works are shown in Table C.2.

Table C.1 Most recent modeling approaches in hydrate phase equilibria.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Temperature (K)</th>
<th>Pressure (MPa)</th>
<th>Study</th>
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<tbody>
<tr>
<td><strong>EoS and Clapeyron eq. based models</strong></td>
<td></td>
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<tr>
<td>Abolala et al.</td>
<td>273.15–292.65</td>
<td>0.56–40.2</td>
<td>The gas hydrate formation conditions of various refrigerants were predicted via the simplified PC-SAFT theory in combination with the Vdw-P model.</td>
</tr>
<tr>
<td>Babaee et al.</td>
<td>268–280</td>
<td>60.1–100.1</td>
<td>The van der Waals–Platteeuw solid solution theory is used for determination of the fugacity of water in hydrate phase. Phase behavior of the hydrogen + water system is modeled using the Valerama–Patel–Teja equation of state (VPT-EoS) with non-density dependent mixing rules. Due to the lack of experimental solubility data of hydrogen in the investigated promoters, the</td>
</tr>
</tbody>
</table>
phase equilibria of the hydrogen + promoter system is treated using the VPT-EoS-GE method consisting the UNIFAC activity model and the modified Huron–Vidal (MHV1) mixing rules.

Clarke and Bishnoi\textsuperscript{226} 264–285.5 0.33–10 The proposed equation of state is based upon contributions to the Helmholtz free energy from a non-electrolyte term and three electrolyte terms. The equation of state is used in conjunction with the Vdw-P model to predict the SVLE conditions.

Eslamimanesh \textit{et al.}\textsuperscript{159} 279–295 0–120 A thermodynamic model is proposed for representation/prediction of phase equilibria of semi-clathrate hydrates. The vDW–P solid solution theory is used, revised with two modifications for evaluations of Langmuir constants and vapor pressure of water in the empty hydrate lattice, in which these values are supposed to be a function of TBAB concentration in aqueous solution. The Peng–Robinson (PR-EoS) equation of state along with retuned parameters of Mathias–Copeman alpha function is applied for calculation of the fugacity of gaseous hydrate former. For determination of the activity coefficient of the non-electrolyte species in the aqueous phase, the non-random two liquid (NRTL) activity model is used.

Eslamimanesh \textit{et al.}\textsuperscript{227} 276–294 2–500 The model based on conventional Clapeyron model. Considering that the effect of pressure on molar volume of gas hydrate could not ignored, the “Clausius–Clapeyron” equation was improved from \(\frac{dp}{dT} = \frac{\Delta H_\text{d}}{T} \frac{dV}{dV}\) to \(\frac{dp}{dT} = \frac{\Delta H_\text{f} + n_x \Delta H_\text{f}}{T} \frac{dV}{dV}\).

Eslamimanesh \textit{et al.}\textsuperscript{151} 273.2–292 1.35–101 The PR EoS and NRTL activity model are applied for modeling the fluid phases. The vDW–P theory along with two modifications is used for hydrate phase.

Eslamimanesh \textit{et al.}\textsuperscript{228} 248.15–298.15 0.008–439 A statistical method for diagnostics of the outliers in phase equilibrium data (dissociation data) of simple clathrate hydrates is presented. The applied algorithm is performed on the basis of the Leverage mathematical approach, in which the statistical Hat matrix, Williams Plot, and the residuals of a selected correlation results lead to define the probable outliers.
**Appendices**

<table>
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<tr>
<th>Author(s)</th>
<th>Temperature Range</th>
<th>Enthalpy Range</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>Fan et al.</td>
<td>267.2–279.7</td>
<td>0.8–3.5</td>
<td>The hydrate models recently developed by this group (Chen–Guo and Zuo–Guo model) and a typical literature reported Vdw-P type model were tested.</td>
</tr>
<tr>
<td>Fukumoto et al.</td>
<td>275–300</td>
<td>0–5</td>
<td>The model proposed by Paricaud\textsuperscript{112} is applied. The SAFT-VRE equation of state is used to describe the properties of fluid phases. Group contribution methods are proposed to predict the fusion enthalpies and the congruent melting points of semicladrate hydrates. The vdw-P theory is combined with the model to calculate the dissociation conditions of carbon dioxide semicladrate hydrates.</td>
</tr>
<tr>
<td>Fukumoto et al.</td>
<td>282.31–289.75</td>
<td>0–16</td>
<td>The model proposed by Paricaud\textsuperscript{112} is applied to predict the dissociation condition of the H\textsubscript{2} semicladrate hydrate with TBAC. The parameters in the model have been determined by describing the liquid–vapor–hydrate three phase lines measured in this work and from the literature.</td>
</tr>
<tr>
<td>Fukumoto et al.</td>
<td>273–303</td>
<td>0–30</td>
<td>The model proposed by Paricaud\textsuperscript{112} is applied to predict the dissociation condition of the H\textsubscript{2}+CO\textsubscript{2} semicladrate hydrates with TBA salts and TBPB.</td>
</tr>
<tr>
<td>Illbeigi et al.</td>
<td>274.2–296.48</td>
<td>1.06–14.05</td>
<td>The thermodynamic model is based on the Vdw-P solid solution theory combined with an equation of state and activity model. The Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) equations of state with random mixing rules are used to model the gas phase, while the UNIFAC method is used to model the liquid phase(s).</td>
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<tr>
<td>Herri et al.</td>
<td>273.2–280</td>
<td>1.39–32.31</td>
<td>The data have been described by means of the vdW-P model in which the Kihara parameters had been recalculated for an optimized set of macroscopic parameters taken from Handa and Tse\textsuperscript{231}.</td>
</tr>
<tr>
<td>Javanmardi et al.</td>
<td>263–279</td>
<td>0.9–3.0</td>
<td>This method uses a generalization of the Aasberg-Petersen model\textsuperscript{233} for water activity. Calculated values of the hydrate formation temperature in the presence of alcohols and electrolytes are compared with those obtained by other existing models.</td>
</tr>
<tr>
<td>Jager and Sloan</td>
<td>267–302</td>
<td>6.6–72.26</td>
<td>Calculations have been done on literature data for methane hydrate and new data. Both the Clapeyron relation and Vdw-P hydrate theory has been used.</td>
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<tr>
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<td>Description</td>
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<tr>
<td>Kim <em>et al.</em> 235</td>
<td>272–286</td>
<td>1.2–24.1</td>
<td>Complex phase behaviors composed of two-, three- and four- phases were observed and they were analyzed by comparing with calculations using GSMGem program developed by Sloan and Koh 24.</td>
</tr>
<tr>
<td>Klauda and Sandler 236</td>
<td>273.1–304.9</td>
<td>1–100</td>
<td>A fugacity-based model is developed for the prediction of equilibrium pressures and cage occupancies of pure and mixed component hydrates.</td>
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<tr>
<td>Larson 122</td>
<td>257–283</td>
<td>0.5–4.5</td>
<td>Predicted the equilibrium hydrate formation conditions of CO2 hydrates.</td>
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<tr>
<td>Li and Englezos 237</td>
<td>298–313</td>
<td>5.0–11.0</td>
<td>SAFT equation of state was employed for the correlation and prediction of vapor–liquid equilibrium of eighteen binary mixtures. The predicted values agreed with the experimental data except for the H2O–CH3OH–CH4 at low CH3OH concentration in liquid phase of 60 wt%.</td>
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<tr>
<td>Mei <em>et al.</em> 238</td>
<td>268.1–285.8</td>
<td>2.05–12.68</td>
<td>The generalized hydrate model proposed recently by this group was used to predict the hydrate formation conditions.</td>
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<td>Moradi and Khosravani 239</td>
<td>232.6–398.15</td>
<td>0.185–20.51</td>
<td>The model is based on equality of water fugacity in the liquid water and hydrate phases. The Vdw-P model is applied for calculating the fugacity of water in the hydrate phase. The Stryjek and Vera modification of Peng–Robinson (PRSV2) equation of state is used to evaluate the fugacity of water in the vapor and liquid phases.</td>
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<tr>
<td>Moradi and Khosravani 240</td>
<td>274.14–398.15</td>
<td>0.0053–827</td>
<td>The vdW-P model is applied for calculating the fugacity of water in the hydrate phase. The Stryjek and Vera modification of Peng–Robinson (PRSV2) equation of state is used to evaluate the fugacity of water in the vapor and liquid phases.</td>
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<tr>
<td>Osfouri <em>et al.</em> 241</td>
<td>259.0–285.2</td>
<td>1.1–23</td>
<td>The proposed model is based on the γ–φ approach, which uses modified Patel–Teja equation of state (VPT EoS) for characterizing the vapor phase, the solid solution theory by vDW-P for modeling the hydrate phase, the non-electrolyte NRTL-NRF local composition model and Pitzer–Debye–Huckel equation as short-range and long-range contributions to calculate water activity in single electrolyte solutions. Also, the Margules equation was used to determine the activity of water in solutions containing polar inhibitor (glycols).</td>
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<td>Pahlavanzadeh et al.</td>
<td>271.5–305</td>
<td>1–55</td>
<td>The solid solution theory of Vdw-P is used for calculating the fugacity of water in the hydrate phase. The UNIFAC group contribution model is used to calculate the water and THF, 1,4-dioxane or acetone fugacities in the aqueous phase.</td>
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<tr>
<td>Paricaud</td>
<td>223–315</td>
<td>0–30</td>
<td>A thermodynamic approach is proposed to determine the dissociation conditions of salt hydrates and semiclaathrate hydrates. The thermodynamic properties of the liquid phase are described with the SAFT-VR equation of state, and the solid-liquid equilibria are solved by applying the Gibbs energy minimization criterion under stoichiometric constraints. The vdW-P theory combined with the new model for salt hydrates is used to determine the dissociation temperatures of semiclaathrate hydrates.</td>
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<td>Ramana Avula et al.</td>
<td>272.9–291.59</td>
<td>2.48–20.78</td>
<td>The hydrate phase is computed from modified vdW–P model. The Peng–Robinson equation of state (PR-EoS) and developed activity model as a combination of Pitzer–Mayorga–Zavitsas-hydration model is used to evaluate the fugacities of gas and liquid phases, respectively. The hydrate phase stability prediction is also computed using the liquid phase activity predicted by NRTL and Pitzer–Mayogra models, separately, and is compared with the results predicted from the developed model.</td>
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<td>Renault-Crispo et al.</td>
<td>274.19–444.26</td>
<td>0.6–68.9</td>
<td>This work demonstrates the sensitivity and importance of the liquid phase compositions on selected models and parameters. The equations of state used to model two-phase systems are the Soave–Redlich–Kwong, the Valderrama–Patel–Teja and the Trebble–Bishnoi equations of state. The modeling analysis for three-phase systems is based on the Trebble–Bishnoi equation of state along with the model by Vdw-P.</td>
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<td>Robinson and Mehta</td>
<td>274–283</td>
<td>1.3–4.5</td>
<td>The conditions for initial hydrate formation in the system of CO$_2$–C$_3$H$_8$–H$_2$O over a wide concentration range for the hydrate-water-rich liquid–gas phase region were measured and predicted in terms of solid–vapor K-factor.</td>
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<td>Seo and Lee, Seo et al.</td>
<td>272–284</td>
<td>1.5–5.0</td>
<td>The three phase equilibria for aqueous phase containing CO$_2$ and CH$_4$ were predicted. The vapor and liquid phases were treated with SRK-EoS incorporated with the second-order modified Huron–Vidal (MHV2) mixed</td>
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</table>
rule and hydrate phase with the Vdw-P model.

Seo et al.\textsuperscript{163} 255–284.53 0.807–10.5 Hydrate phase equilibria data modeled based on Vdw-P model\textsuperscript{23}. The fugacities of supercooled water and all components in the vapor phase were calculated using the Soave-Redlich-Kwong (SRK) equation of state incorporated with the modified Huron-Vidal second order mixing rule.

Seo et al.\textsuperscript{164} 280.56–302.46 1.74–11.84 A new thermodynamic model was developed to describe the phase equilibria of mixed hydrates containing two guest molecules. The Soave–Redlich–Kwong equation of state (SRK EoS) was used with the modified Huron–Vidal (MHV2) mixing rule incorporated with the modified UNIFAC.

Sfaxi et al.\textsuperscript{161} 278.1–285.3 3.24–29.92 A thermodynamic model based on the CPA equation of state for fluid phases combined with the Vdw-P solid solution theory for the hydrate phase is presented. The dissociation data generated in this work along with the experimental data reported in the literature are compared with the results of this model and also with the predictions of two other thermodynamic models, namely HWHYD and CSMGem.

Sun and Chen\textsuperscript{245} 273.5–299.7 0.5–8.5 By introducing Debye–Huckel electrostatic contribution term, their method coupled with Chen–Guo model was successfully used to predict the thermodynamics property of hydrates.

Sun and Duan\textsuperscript{246}, Duan and Sun\textsuperscript{247} 253–293 0.5–200 Ab initio potential model predicting initial hydrate formation conditions for CH\textsubscript{4} and CO\textsubscript{2}. Compared to the models employing the Kihara potential or Lennard-Jones potential, atomic site–site potentials were more accurate either under low pressure or under high pressure.

Tavasoli et al.\textsuperscript{248} 273.2–310.3 0.2–100 Elliott–Suresh–Donohue (ESD) equation of state (EoS) which is based on thermodynamic perturbation theory and uses the Wertheim association contribution to account for association interactions, is applied to predict hydrate formation conditions in the presence and absence of thermodynamic inhibitors. The ESD EoS is coupled with the Vdw-P model.

Tsimpanogiannis \textit{et al.}\textsuperscript{249} 270–310 20–500 Novel Grand Canonical Monte Carlo molecular simulations are applied for the case of pure s(II) N\textsubscript{2} hydrate. The simulation
compares the calculated cavity occupancies with experimental data and observes reasonable agreement.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Temperature</th>
<th>Pressure Range</th>
<th>Gas Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tumba et al.</td>
<td>275–285</td>
<td>1.52–16.23</td>
<td>A thermodynamic model, developed based on Vdw-P solid solution theory accompanied with the Peng-Robinson equation of state (PR-EoS) and the non random two-liquid (NRTL) activity model, was successfully applied to represent/predict the obtained experimental data.</td>
</tr>
<tr>
<td>Valavi and Dehghan</td>
<td>263.3–300.9</td>
<td>0.1–9</td>
<td>The modified PHSC (Perturbed hard sphere chain) EoS has been employed to predict the hydrate formation conditions of pure gases as well as their gas mixtures in the presence and absence of thermodynamic inhibitors, electrolytes, mixed electrolytes and mixture of inhibitor–electrolytes.</td>
</tr>
<tr>
<td>Yang et al.</td>
<td>240–298.2</td>
<td>1.1–19.4</td>
<td>Applicability of the lattice fluid equation of state by the present authors was also investigated for the unified description of various phase equilibria with Langmuir constants in the Vdw-P model for hydrates and hydrogen-bonding free energy of water fitted to data, the model was found to consistently describe various two- and three-phase equilibria.</td>
</tr>
<tr>
<td>Yoon et al.</td>
<td>205–295</td>
<td>0.01–69</td>
<td>A generalized hydrate equilibrium model was developed for accurately predicting the complete phase behavior of simple and mixed hydrate systems. The fugacities of all components in the vapor and liquid phases coexisting with hydrates were calculated by using the SRK-EoS incorporated with the MHV2 mixing rule. The UNIFAC group contribution model was also used as the excess Gibbs energy for the MHV2 model.</td>
</tr>
</tbody>
</table>

**Gas gravity methods and correlation based methods**

<table>
<thead>
<tr>
<th>Authors</th>
<th>Temperature</th>
<th>Pressure Range</th>
<th>Gas Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ameripour and Barrufet</td>
<td>&lt;305.38</td>
<td>&lt;82.7</td>
<td>Two correlations calculate the hydrate formation pressure or temperature for single components or gas mixtures, with or without inhibitors.</td>
</tr>
<tr>
<td>Bahadori and Vuthaluru</td>
<td>265–298</td>
<td>1.2–40.0</td>
<td>A novel correlation based on the extracted data from Katz gas-gravity charts was proposed to predict the hydrate formation conditions for gases.</td>
</tr>
<tr>
<td>Eslamimanesh et al.</td>
<td>265.31–283.49</td>
<td>0.007–1.489</td>
<td>A thermodynamic model is presented for the study of the phase equilibria of clathrate hydrates of simple refrigerants. The Vdw-P</td>
</tr>
</tbody>
</table>
solid solution theory is used to model the hydrate phase.

**Holder et al.**\(^ {172} \) - - Empirical correlations developed in different forms and with various numbers of parameters.

**Hosseini-Nasab et al.**\(^ {255} \)

\[270.9 - 300\] \([3-31]\) The authors employed SAS (SAS Institute, Cary, North Carolina) to develop a correlation for predicting the hydrate-formation temperatures for both pure and mixture of hydrocarbon systems using the gravity method. The method correlates the hydrate-formation pressure against specific gravity, pressure, and water-vapor pressure.

**Omole et al.**\(^ {256} \) - - This study employed Statistical Analysis Software (SAS) to develop a new correlation for predicting the hydrate formation temperatures for both pure and mixture of hydrocarbon systems using gravity method. The method correlates the hydrate-formation pressure against specific gravity, pressure and water-vapour pressure.

**Rashidabad et al.**\(^ {257} \)

\[263.2 - 281.7\] \([2.5-9.5]\) A 10 variable linear regression model was offered for thermodynamic model of hydrate formation of methane in the presence of electrolytes and the obtained data was compared with the model calculations numerical results.

**Table C.2** Average standard pressure/temperature deviations of modeling results from literature.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Systems</th>
<th>Average standard pressure deviation (AAPD) (%)</th>
<th>Average standard temperature deviation (AATD) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abolala et al.(^ {216} )</td>
<td>Refrigerants</td>
<td>1.15</td>
<td>–</td>
</tr>
<tr>
<td>Babaee et al.(^ {217} )</td>
<td>Derivatives of butane, pentane, cyclopentane and cyclohexane</td>
<td>–</td>
<td>0.06</td>
</tr>
<tr>
<td>Eslamimanesh et al.(^ {219} )</td>
<td>CO(_2)</td>
<td>1.8</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>CH(_4)</td>
<td>2.3</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>N(_2)</td>
<td>4</td>
<td>–</td>
</tr>
<tr>
<td>Eslamimanesh et al.(^ {222} )</td>
<td>R-134a</td>
<td>4.9*</td>
<td>5.3**</td>
</tr>
<tr>
<td></td>
<td>R-141b</td>
<td>0.1*</td>
<td>10**</td>
</tr>
<tr>
<td></td>
<td>R-152b</td>
<td>16* [s(II)] 30** [s(II)]</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>R-32</td>
<td>1.8*</td>
<td>0.6**</td>
</tr>
<tr>
<td>Authors</td>
<td>Reactions</td>
<td>ΔG (kJ/mol)</td>
<td>ΔH (kJ/mol)</td>
</tr>
<tr>
<td>------------------</td>
<td>---------------------------------------------------------------------------</td>
<td>-------------</td>
<td>-------------</td>
</tr>
<tr>
<td>Fan et al.</td>
<td>(CO_2 + \text{N}_2/\text{CH}_4/\text{C}_2\text{H}_6/\text{MEG/MeOH})</td>
<td>4.82</td>
<td>7.92</td>
</tr>
<tr>
<td>Fukumoto et al.</td>
<td>TBAB + CO_2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>TBAC + CO_2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>TBAF + CO_2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>TBPB + CO_2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Fukumoto et al.</td>
<td>TBAC</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Illbeigi et al.</td>
<td>CH_4 + (CC6 or derivatives)/CP/aceton e/1,4-dioxane</td>
<td>3.99</td>
<td>4.35</td>
</tr>
<tr>
<td>Herri et al.</td>
<td>CO_2/CO_2/CO_2 + CH_4</td>
<td>976.7</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>CO_2/\text{N}_2/CO_2 + N_2</td>
<td>393.2</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>N_2</td>
<td>16.64</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>N_2/\text{CH}_4/ N_2 + CH_4</td>
<td>123.7</td>
<td>–</td>
</tr>
<tr>
<td>Javanmardi et al.</td>
<td>CO_2 + \text{CH}_4/\text{H}_2\text{S}/\text{C}_2\text{H}_6/\text{CH}_4+\text{TH}_3\text{H}_4/ + \text{MeOH}</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Kim et al.</td>
<td>CO_2 + N_2</td>
<td>11.9</td>
<td>19.4</td>
</tr>
<tr>
<td>Klauda and</td>
<td>NG single components</td>
<td>20.4</td>
<td>–</td>
</tr>
<tr>
<td>Sandler</td>
<td>NG binary and ternary systems</td>
<td>11.6</td>
<td>–</td>
</tr>
<tr>
<td>Mei et al.</td>
<td>CO_2 + CH_4 (+salts)</td>
<td>13.96</td>
<td>–</td>
</tr>
<tr>
<td>Moradi and</td>
<td>NG single components</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Khosravani</td>
<td>NG ternary and quaternary systems with MeOH/MEG</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Moradi and</td>
<td>NG single components</td>
<td>11.15</td>
<td>–</td>
</tr>
<tr>
<td>Khosravani</td>
<td>NG binary, ternary and quaternary systems</td>
<td>13.25</td>
<td>–</td>
</tr>
<tr>
<td>Osfouri et al.</td>
<td>NG single and binary components + salts</td>
<td>5.86</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>NG single and binary components + mixture of salts</td>
<td>5.23</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>NG single components + MEG+NaCl/\text{CaCl}_2/(\text{NaCl}+\text{CaCl}_2)</td>
<td>14.13</td>
<td>–</td>
</tr>
<tr>
<td>Paricaud</td>
<td>CO_2+HI/LiBr/TBAB</td>
<td>10.5</td>
<td>–</td>
</tr>
<tr>
<td>Sun and Chen</td>
<td>NG ternary and quaternary systems</td>
<td>5.89</td>
<td>–</td>
</tr>
<tr>
<td>Tavasoli et al.</td>
<td>NG ternary, quaternary and multicomponent systems</td>
<td>9.75</td>
<td>–</td>
</tr>
</tbody>
</table>
Appendices

NG ternary systems with MEG/MeOH/EtOH
Valavi and Dehghani\textsuperscript{249} 6.98
NG ternary systems
6.15
NG ternary systems with salt
5.82
NG quaternary systems with mixture of salts
6.80
NG single components + MeOH + salt
7.56
Yang \textit{et al.} \textsuperscript{250} CH\textsubscript{4} + H\textsubscript{2}O 25.50
Yoon \textit{et al.} \textsuperscript{251} NG single components 3.41

*Absolute average deviations of the calculated hydrate dissociation pressures.
**Absolute average deviations of the predicted hydrate dissociation pressures.
\textsuperscript{a}AAD based on Chen and Guo model\textsuperscript{223, 233, 234}.
\textsuperscript{b}AAD based on Zuo and Guo model\textsuperscript{223, 233, 234}.
\textsuperscript{c}AAD based on CSMHYD model\textsuperscript{24, 166, 223}.
\textsuperscript{d}Maximum AAD \% values are mentioned.
\textsuperscript{e}Fluid phase is modeled by SRK.
\textsuperscript{f}Fluid phase is modeled by PR.
\textsuperscript{g}Fluid phase model is taken from literature.

Appendix D

The different Kihara parameters in literature and the EoS used to calculate them are presented in Table D.1.

Table D.1 Kihara parameters for the compounds examined in this work.

<table>
<thead>
<tr>
<th>Component</th>
<th>$a \cdot 10^{10}$ (m)</th>
<th>$\sigma \cdot 10^{10}$ (m)</th>
<th>$\varepsilon/k_B$ (K)</th>
<th>EoS used for fugacity calculation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>0.6805</td>
<td>2.9643</td>
<td>171.70</td>
<td>a parameter is obtained from Sloan and Koh\textsuperscript{258} and $\sigma$, $\varepsilon$ are correlated</td>
<td>Herslund\textsuperscript{20}</td>
</tr>
<tr>
<td></td>
<td>0.6805</td>
<td>2.97638</td>
<td>175.405</td>
<td>CSMHYD/CSMGem</td>
<td>Sloan and Koh\textsuperscript{24}</td>
</tr>
<tr>
<td></td>
<td>0.7530</td>
<td>2.349</td>
<td>420.300</td>
<td>Valderrama-Patel-Teja (VPT EoS) with non-density-dependent mixing rules</td>
<td>Avlonitis\textsuperscript{259}</td>
</tr>
<tr>
<td></td>
<td>0.6805</td>
<td>2.9818</td>
<td>168.77</td>
<td>CSMHYD</td>
<td>Sloan\textsuperscript{174}</td>
</tr>
<tr>
<td></td>
<td>0.7200</td>
<td>2.9681</td>
<td>169.09</td>
<td>modified Redlich-Kwong</td>
<td>Parrish and Prausnitz\textsuperscript{166}</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.3526</td>
<td>3.1723</td>
<td>128.07</td>
<td>Soave-Redlich-Kwong</td>
<td>Strobel \textit{et al.} \textsuperscript{181}</td>
</tr>
<tr>
<td></td>
<td>0.3526</td>
<td>3.13512</td>
<td>127.426</td>
<td>CSMHYD/CSMGem</td>
<td>Sloan and Koh\textsuperscript{24}</td>
</tr>
<tr>
<td>Compound</td>
<td>Volume (m³/m³)</td>
<td>Density (g/mL)</td>
<td>Temperature (°C)</td>
<td>Equation/Model</td>
<td></td>
</tr>
<tr>
<td>--------------------------</td>
<td>---------------</td>
<td>---------------</td>
<td>------------------</td>
<td>-----------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>0.8968</td>
<td>3.1480</td>
<td>250.89</td>
<td>CSMHYD</td>
<td></td>
</tr>
<tr>
<td>Methyl-Cyclopentane (mCP)</td>
<td>1.0054</td>
<td>4.5420</td>
<td>353.66</td>
<td>CSMHYD</td>
<td></td>
</tr>
<tr>
<td>Ethyl-cyclopentane (eCP)</td>
<td>1.1401</td>
<td>3.60425</td>
<td>219.083</td>
<td>CSMHYD/CSMGem</td>
<td></td>
</tr>
<tr>
<td>Cyclohexane (CC6)</td>
<td>0.9750</td>
<td>4.2675</td>
<td>253.00</td>
<td>modified PVT with non-density-dependent mixing rules</td>
<td></td>
</tr>
<tr>
<td>Methyl-Cyclohexane (mCC6)</td>
<td>1.0693</td>
<td>3.1931</td>
<td>407.29</td>
<td>CSMHYD</td>
<td></td>
</tr>
<tr>
<td>Cycloheptane (CC7)</td>
<td>1.0576</td>
<td>3.5902</td>
<td>250.19</td>
<td>CSMGem</td>
<td></td>
</tr>
<tr>
<td>Cyclooctane (CC8)</td>
<td>1.1048</td>
<td>3.6550</td>
<td>277.80</td>
<td>CSMGem</td>
<td></td>
</tr>
<tr>
<td>Methyl-Cyclooctane (mCC8)</td>
<td>1.1048</td>
<td>3.6337</td>
<td>277.80</td>
<td>CSMHYD</td>
<td></td>
</tr>
</tbody>
</table>

Valderrama-Patel-Teja with non-density-dependent mixing rules

Avlonitis²⁵⁹

Tohidi et al.¹⁷⁴

CSMHYD

Mehta and Sloan¹⁷⁹, Sloan¹⁷⁴

modified Redlich-Kwong

Parrish and Prausnitz¹⁰⁶

Sloan¹⁷⁴

CSMHYD/CSMGem

Sloan and Koh²⁴

Peng-Robinson

Ma et al.²⁶⁰

CSMHYD/CSMGem

Sloan and Koh²⁴

CSMHYD

Mehta and Sloan¹⁷⁹

Parrish and Prausnitz¹⁰⁶

Modified PVT with non-density-dependent mixing rules

Tohidi et al.¹⁷⁴

CSMHYD

Mehta and Sloan¹⁷⁹

Peng-Robinson

Ma et al.²⁶⁰

CSMHYD/CSMGem

Sloan and Koh²⁴

CSMGem

Sloan and Koh²⁴

Peng-Robinson

Ma et al.²⁶⁰

CSMGem

Sloan and Koh²⁴; Ma et al.²⁶⁰

CSMHYD

Mehta and Sloan¹⁷⁹

CSMGem

Sloan and Koh²⁴
Appendix E

E.1 Contributions to Conferences

International Conferences


Internal Meetings

Tzirakis F., von Solms N., Kontogeorgis G., Coquelet C., Stringari P., Hydrate equilibrium data for CO\(_2\)+N\(_2\) system with the use of TBAB, TBAF, CP, TBAB+CP, TBAF+CP (*Oral*), CERE Annual Discussion Meeting, Snekkersten, Denmark, June 25\(^{th}\)-27\(^{th}\), 2014.

Tzirakis F., von Solms N., Kontogeorgis G., Coquelet C., Stringari P., Hydrate equilibrium data for CO\(_2\)+N\(_2\) system with the use of pressure reduction chemicals (promoters) (*Oral*), CERE Annual Discussion Meeting, Snekkersten, Denmark, June 17\(^{th}\)-19\(^{th}\), 2015.
Tzirakis F., von Solms N., Kontogeorgis G., Coquelet C., Stringari P., Hydrate equilibrium data and modeling of CO$_2$-cyclo-alkane hydrates (Oral), CERE Annual Discussion Meeting, Helsingør, Denmark, June 15$^{th}$-17$^{th}$, 2016.

Tzirakis F., von Solms N., Kontogeorgis G., Coquelet C., Stringari P., Experiments for CO$_2$ hydrates – promoters (Poster), CERE Annual Discussion Meeting, Snekkersten, Denmark, June 19$^{th}$-21$^{th}$, 2013.

Tzirakis F., von Solms N., Kontogeorgis G., Coquelet C., Stringari P., Experimental hydrate promotion data for CO$_2$+N$_2$+TBAB+H$_2$O system (Poster), CERE Annual Discussion Meeting, Snekkersten, Denmark, June 25$^{th}$-27$^{th}$, 2014.

Tzirakis F., von Solms N., Kontogeorgis G., Coquelet C., Stringari P., Hydrate equilibrium data for CO$_2$+N$_2$ system with the use of pressure reduction chemicals (promoters) (Poster), CERE Annual Discussion Meeting, Snekkersten, Denmark, June 17$^{th}$-19$^{th}$, 2015.

Tzirakis F., von Solms N., Kontogeorgis G., Coquelet C., Stringari P., Experimental uncertainties of hydrate equilibrium data (Poster), CERE Annual Discussion Meeting, Snekkersten, Denmark, June 17$^{th}$-19$^{th}$, 2015.

D.2 List of Publications

Tzirakis F., Stringari P., von Solms N., Coquelet C., Kontogeorgis G., Hydrate equilibrium data for the CO$_2$+N$_2$ system with the use of Tetra-n-butylammonium bromide (TBAB), cyclopentane (CP) and their mixture, *Fluid Phase Equilib.*, 2016, 408, 240-247.


D.3 Distinction

Otto Mønsteds Foundation grant for ESAT and ICCDU conferences (2015)

D.4 Attended Courses

- Advanced Raman Spectroscopy (10 ECTS)
- Thermodynamic Models, Fundamentals and Computational Aspects (7.5 ECTS)
- Advances in Chemical and Biochemical Engineering (2.5 ECTS)
- Phase Equilibria for Separation Processes (5 ECTS)
• Environmental Economics (5 ECTS)

Ἀληθῶς, Κύριε, ἐάν μὴ ταπεινωθῶμεν, οὐ παύῃ ταπεινῶν ἡμᾶς.