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HYDRATE DISSOCIATION CONDITIONS AT HIGH PRESSURE: EXPERIMENTAL EQUILIBRIUM DATA AND THERMODYNAMIC MODELLING

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ABSTRACT

The past decade has witnessed dramatic changes in the oil and gas industry with the drilling and production extending into progressively deeper waters and higher operating pressures, therefore making it essential to gain a better understanding of the behaviour of gas hydrate at high pressure conditions.

New experimental 3-phase H−L_W−V (Hydrate−Liquid Water−Vapour) equilibrium data for nitrogen and H−L_W−V (Hydrate−Liquid Water−Vapour) and H−L_W−L_{HC} (Hydrate−Liquid Water−Liquid Hydrocarbon) data for ethane and propane simple clathrate hydrates were generated by a reliable fixed-volume, isochoric, step-heating technique. The accuracy and reliability of the experimental measurements are demonstrated by comparing measurements with reliable literature data from different researchers. Additional experimental data up to high pressure (200 MPa when available) for CH_4, C_2H_6, C_3H_8, i-C_4H_{10}, N_2, Ar, Kr, Xe, H_2S, O_2, CO and CO_2 clathrates have been gathered from literature.

The Valderrama modification of the Patel-Teja (VPT) equation of state combined with non-density-dependent (NDD) mixing rules is used to model the fluid phases with previously reported binary interaction parameters. The hydrate-forming conditions are modelled by the solid solution theory of van der Waals and Platteeuw. Langmuir constants have been calculated by both Kihara potential as well as direct techniques. Model predictions are validated against independent experimental data and a good agreement between predictions and experimental data is observed, supporting the reliability of the developed model.

Keywords: Gas hydrate, equation of state, methane, ethane, propane, butane, nitrogen, argon, krypton, xenon, hydrogen sulphide, oxygen, carbon monoxide, carbon dioxide, experimental data.

NOMENCLATURE

BIP	Binary interaction parameter
C	Langmuir constant
EoS	Equation of state
f	Fugacity
HC	Hydrocarbon
NDD	Non density dependent mixing rules
P	Pressure [MPa]
sI	Structure-I
sII	Structure-II
T	Temperature [K]
$\bar{v}$	Number of cavities per water molecule in the unit cell
VPT	Valderrama modification of Patel-Teja

Superscript

H	Hydrate
L	Liquid state
m	Cavity type
Ref	Reference property
V	Vapour state

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Subscripts

0	Reference property
exp	Experimental property
i, j	Molecular species
HC	Hydrocarbon component
W	Water

Greek

α	Kihara hard-core radius
β	Refer to empty hydrate lattice
ε	Kihara energy parameter
θ	Occupancy of the cavity
k	Boltzmann's Constant
σ	Kihara collision diameter
$\Delta C'_{pw}$	Heat capacity difference between the empty hydrate lattice and liquid water
$\Delta\mu^{\circ}_{w}$	Chemical potential difference between the empty hydrate lattice and ice at ice point and zero pressure
w	The spherically symmetric cell potential in the cavity

INTRODUCTION

Gas hydrates and crystalline compounds that can form when water or ice and suitably sized molecules are brought together under favourable conditions, usually at low temperatures and elevated pressures. Gas hydrates could form in numerous hydrocarbon production and processing operations, causing serious operational and safety concerns, therefore making it essential to gain a better understanding of the behaviour of gas hydrate.

Most of the existing experimental gas hydrate data for real reservoir fluids are limited to low to medium pressure conditions. This is partly due to a lack of interest/application at high pressure conditions and also due to practical difficulties when conducting such measurements. However, production from deeper water reservoirs, and the need for long tie backs, necessitates hydrate prevention at high pressure conditions. With the increasing number of deep offshore drilling operations, high pressure tests on formation of gas hydrates in drilling muds and/or hydraulic fluids are necessary as operators and service companies have to solve more and more complex technical challenges. Extreme conditions encountered at these depths require an adaptation of the drilling muds, hydraulic fluids, and oilfield chemicals to ensure hydrate formation is not an issue. Furthermore the limited data that is available in the literature is scattered and shows some discrepancies, highlighting the need for reliable measurements [1]. In this work, the hydrate dissociation point measurements were determined for simple nitrogen, ethane and propane hydrates from medium to high pressure. These data were used in the development and validation of the presented predictive techniques.

In this work, the statistical model uses the Valderrama modification of Patel and Teja equation of state (VPT EoS) for fugacity calculations in all phases [2]. Non density dependent (NDD) mixing rules are applied to model interaction between molecules [3]. The hydrate-forming conditions are modelled by the solid solution theory of van der Waals and Platteeuw. Langmuir constants have been calculated by both Kihara potential as well as direct techniques. The performance of the model has been tested by comparing the predictions with the data generated in this laboratory as well as the most reliable data from the open literature for hydrate stability zone.

EXPERIMENTAL

Clathrate dissociation PT conditions were determined by standard constant volume cell isochoric equilibrium step-heating techniques. This method, which is based upon the direct detection (from pressure) of bulk density changes occurring during phase transitions, produces very reliable, repeatable phase equilibrium measurements [4].

Materials

Nitrogen, ethane and propane were purchased from BOC gases with a certified purity greater than 99.995 vol. %. Aqueous solutions were prepared using deionized water throughout the experimental work.

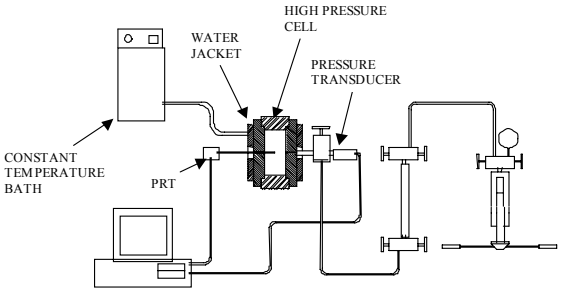

Figure 1 Schematic of ultra high pressure rig

Ultra-High Pressure Apparatus

The 'ultra-high pressure' hydrate set-up was used for tests up to 200 MPa. It is comprised of a 45 ml cell constructed of AISI 660 steel. A schematic of the set-up is shown in Figure 1. The cell has been pressure tested to 200 MPa and can be used with salts and organic hydrate inhibitors. The cell temperature is monitored with a PRT (Platinum Resistance Thermometer) with the sensing part in contact with test fluids. The cell pressure is measured using a *Quartzdyne* pressure transducer accurate to 0.05 MPa. The system temperature is controlled by circulating coolant from a cryostat through a jacket surrounding the cell. Mixing is achieved by rocking the cell through 180° using a compressed air-driven mechanism. To aid mixing, two steel ball-bearings are placed inside the cell.

THERMODYNAMIC MODELLING

For a system at equilibrium, from a thermodynamic point of view, the criterion for phase equilibrium is the equality of chemical potentials of each component in all coexisting phases. For an isothermal system this will reduce to the equality of fugacity of each component in different phases. A general phase equilibrium model based on equality of fugacity of each component throughout all the phases [5, 6] is used to model the equilibrium conditions. The VPT – EoS [2] with NDD mixing rules [3] is used to determine component fugacities in fluid phases. This combination has proven to be a strong tool in modelling systems with polar as well as non-polar compounds [3]. The hydrate-forming conditions are modelled by the solid solution theory of van der Waals and Platteeuw [7]. Langmuir constants have been calculated by both Kihara potential as well as direct techniques.

Modelling of hydrate phase

The statistical thermodynamic model of van der Waals and Platteeuw [7] provides a bridge between the microscopic properties of the clathrate hydrate structure and macroscopic thermodynamic properties, i.e., the phase behaviour. The hydrate phase is modelled by using the solid solution theory of van der Waals and Platteeuw [7], as implemented by Parrish and Prausnitz [8]. The fugacity of water in the hydrate phase is given by the following equation [9]:

$$f_w^H = f_w^\beta \exp\left(-\frac{\Delta\mu_w^{\beta-H}}{RT}\right) \quad (1)$$

where superscripts H and β refer to hydrate and empty hydrate lattice, respectively and μ stands for chemical potential. f_w^β is the fugacity of water in the empty hydrate lattice. $\Delta\mu_w^{\beta-H}$ is the chemical potential difference of water between the empty hydrate lattice, μ_w^β, and the hydrate phase, μ_w^H, which is obtained by the van der Waals and Platteeuw expression:

$$\Delta\mu_w^{\beta-H} = \mu_w^\beta - \mu_w^H = RT\sum_m \bar{v}_m \ln\left(1+\sum_j C_{mj} f_j\right) \quad (2)$$

where $\bar{v}_m$ is the number of cavities of type m per water molecule in the unit cell, f_j is the fugacity of the gas component j. C_{mj} is the Langmuir constant, which accounts for the gas-water interaction in the cavity. The Langmuir constants are temperature dependent functions that describe the potential interaction between the encaged guest molecule and the water molecules surrounding it.

The mechanism of clathrate hydrate formation shows similarities to adsorption of molecules at sites on a surface. The assumptions made for the mechanism of Langmuir adsorption are also applicable for hydrate formation [7, 10]. The occupancy of the sites on a surface in the Langmuir adsorption theory is given by a so-called Langmuir isotherm, which can also be developed for the occupancy of the cavities in clathrate hydrates.

$$\theta_{mj} = \frac{C_{mj} P_m}{1+\sum_m C_{mj} P_m} \quad (3)$$

The Langmuir constant is a direct function of the particle partition function inside the cavity. The Langmuir constant is actually a description of the affinity of the empty cavity for a molecule to occupy this cavity; i.e., the higher the value for the Langmuir constant the more strongly the guest molecule will be encaged. If a potential guest molecule is too large to fit into the cavity, the Langmuir constant will have a value of zero. When the molecule is small related to the size of

the cavity, the Langmuir constant also approaches zero. The relation for the Langmuir constant can be developed from the potential energy and numerical values for the Langmuir constant can be calculated by choosing a model for the guest-host interaction [7]:

$$C_{mj}(T) = \frac{4\pi}{kT}\int_0^{\infty} \exp\left(-\frac{w(r)}{k^{'}T}\right) r^2 dr \qquad (4)$$

where k is Boltzmann's constant. The function $w(r)$ is the spherically symmetric cell potential in the cavity, with r measured from the centre, and depends on the intermolecular potential function chosen for describing the encaged gas-water interaction. In the present work, Langmuir constants have been calculated by both Kihara potential as well as direct techniques.

The Kihara potential function [11] is used as described in McKoy and Sinanoglu [12]. The Kihara potential parameters, α (the radius of the spherical molecular core), σ (the collision diameter), and ε (the characteristic energy) are taken from Tohidi-Kalorazi [13].

For the direct technique, an equation relying on the fitting of the Langmuir constant to experimental hydrate conditions has been applied.

$$C_{mj}(T) = \frac{C_{mj}^{\ 1}}{T}\exp\left(\frac{C_{mj}^{\ 2}}{T}\right) \qquad (5)$$

where $C_{mj}^{\ 1}$ and $C_{mj}^{\ 2}$ are the two adjustable parameters. The fugacity of water in the empty hydrate lattice, f_w^{β} in Equation 1, can be calculated by:

$$f_w^{\beta} = f_w^{I/L}\exp\left(\frac{\Delta\mu_w^{\beta-I/L}}{RT}\right) \qquad (6)$$

where $f_w^{I/L}$ is the fugacity of pure ice or liquid water and $\Delta\mu_w^{\beta-I/LI}$ is the difference in the chemical potential between the empty hydrate lattice and pure liquid water. $\Delta\mu_w^{\beta-I/LI}$ is given by the following equation:

$$\frac{\Delta\mu_w^{\beta-I/L}}{RT} = \frac{\Delta\mu_w^{0}}{RT_0} - \int_{T_0}^{T}\frac{\Delta h_w^{\beta-I/L}}{RT^2}dT + \int_0^{P}\frac{\Delta v_w^{\beta-I/L}}{RT}dP \qquad (7)$$

where superscript *0* stands for reference property and h refers to molar enthalpy. $\Delta\mu_w^{0}$ is the reference chemical potential difference between water in the empty hydrate lattice and pure water at 273.15 K. $\Delta h_w^{\beta-I/L}$ and $\Delta v_w^{\beta-I/L}$ are the molar enthalpy and molar volume differences between an empty hydrate lattice and ice or liquid water. $\Delta h_w^{\beta-I/L}$ is given by the following equation [9, 14]:

$$\Delta h_w^{\beta-I/L} = \Delta h_w^{0} + \int_{T_0}^{T}\Delta C_{Pw}^{'}dT \qquad (8)$$

where C' and subscript P refer to molar heat capacity and pressure, respectively. Δh_w^{0} is the enthalpy difference between the empty hydrate lattice and pure water, at the ice point and zero pressure. The heat capacity difference between the empty hydrate lattice and the pure liquid water phase, $\Delta C_{Pw}^{'}$ is also temperature dependent and the equation recommended by Holder et al. [14] is used:

$$\Delta C_{Pw}^{'} = -37.32 + 0.179(T - T_0) \quad T > T_0 \qquad (9)$$

where $\Delta C_{Pw}^{'}$ is in $Jmol^{-1}K^{-1}$. Furthermore, the heat capacity difference between hydrate structures and ice is set to zero. The reference properties used can be found elsewhere [15].

RESULTS AND DISCUSSIONS

The model described earlier in this paper has been used to model the hydrate phase boundary for the hydrate formers studied in this work. For binary systems containing water and a single hydrate forming compound, the binary interaction parameters are the only adjustable parameters. The binary interaction parameter (BIP) between each component and water has been optimized using aqueous solubility data from open literature and those reported by Avlonitis [5].

The Langmuir constant parameters for each of the hydrate formers studied in this work have been adjusted directly to the most reliable experimental data and reported in Tables 1 and 2 for small and large cavities, respectively. To evaluate the capability of the direct technique for calculating Langmuir constant parameters, assessing the

ability of the model for predicting the hydrate phase equilibria was critical.

	structure	C_{mj}^1 X 1000	C_{mj}^2
C_1	I	6.3077	3068.85
C_2	I	0	0
C_3	II	0	0
i-C_4	II	0	0
N_2	II	23.7420	1987.36
Ar	II	32.9984	1987.38
Kr	II	423.4749	1987.37
Xe	I	1.6574	2459.46
H_2S	I	0.0104	4402.94
O_2	II	602.2165	1275.81
CO	I	0.5497	3000.00
CO_2	I	0.0018	3410.00

Table 1. Langmuir constant parameters for small cavities.

	structure	C_{mj}^1 X 1000	C_{mj}^2
C_1	I	14.4455	2656.58
C_2	I	2.3398	3973.47
C_3	II	1.0852	5192.33
i-C_4	II	177.0000	3900.00
N_2	II	4129.1427	87.20
Ar	II	10693.2764	87.27
Kr	II	2757.6479	87.18
Xe	I	214.8976	3029.80
H_2S	I	21.8438	3764.19
O_2	II	396.19309	592.00
CO	I	2.8945	2833.99
CO_2	I	63.4063	2813.82

Table 2. Langmuir constant parameters for large cavities.

The experimental 3-phase H−L_W−V (Hydrate − Liquid Water − Vapour) equilibrium data for nitrogen and H−L_W−V (Hydrate − Liquid Water − Vapour) and H−L_W−L_{HC} (Hydrate − Liquid Water − Liquid Hydrocarbon) data for ethane and propane simple clathrate hydrates, from this work, are reported in Tables 3 to 5.

T_{exp} / K (±0.1)	P_{exp} / MPa (±0.05)
281.65	38.35
288.95	77.92
289.45	81.33
295.25	134.03
295.05	132.00

Table 3. Results of hydrate dissociation point measurements for nitrogen using the high pressure rig.

T_{exp} / K (±0.2)	P_{exp} / MPa (±0.1)
285.95	2.5
286.45	2.6
288.85	8.2
290.55	19.2
290.75	20.4
291.25	24.3
294.95	55.3
295.15	57
295.25	57.5
295.35	58.7
300.25	107.7
304.35	157.5
304.65	160.6

Table 4. Results of hydrate dissociation point measurements for simple ethane using the high pressure rig.

T_{exp} / K (±0.2)	P_{exp} / MPa (±0.1)
275.35	0.25
276.15	0.31
277.15	0.38
278.65	0.68
278.75	1.48
278.85	2.05
278.95	5.65
279.05	20.54
279.05	29.93
278.95	44.85

Table 5. Results of hydrate dissociation point measurements for simple propane using the high pressure rig.

Figure 1 presents the results of the thermodynamic modelling of the hydrate phase equilibria for methane, ethane, hydrogen sulphide and carbon dioxide and Figure 2 for nitrogen, krypton and xenon. The experimental data measured in this work as well as the most reliable data from literature has been used as a reference for evaluation of the model. Due to the similarity of results for both Kihara potential and the direct technique, only those of the direct technique are presented here. It can be seen that predictions are in good agreement with the experimental data, supporting the reliability of the thermodynamic model.

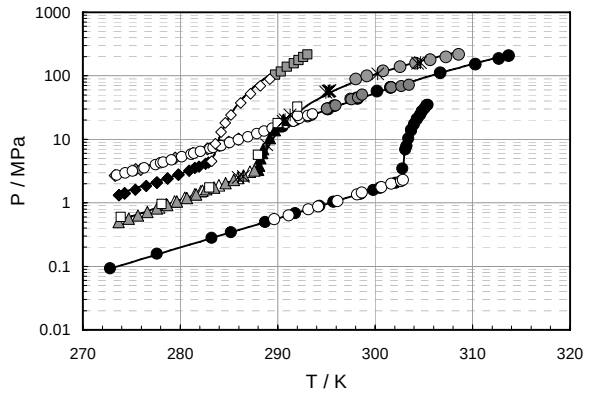

Figure 1 Experimental and predicted simple hydrate dissociation conditions. Experimental data for methane hydrate from: (●) Marshall et al. [16], (◆) De Roo et al. [17], (●) Jagerand and Sloan [18], and (○) Nixdorf and Oellrich [19]. Experimental data for ethane hydrate from: (△) Avlonatis [5], (▲) Ng and Robinson [20], (■) Morita et al. [21], (▲)Nixforf and Ollrich [19], (□) Ross and Toczylkin [22], and (✱) this work. Experimental data for hydrogen sulphide hydrate from: (●) Selleck et al. [23], and (○) Scheffer and Meyer [24]. Experimental data for carbon dioxide hydrate from: (◆) Deaton and Frost [25], (■) Nakano et al. [26], (◇) and Takenouchi and Kennedy [27]. Black lines are the predictions of the developed model.

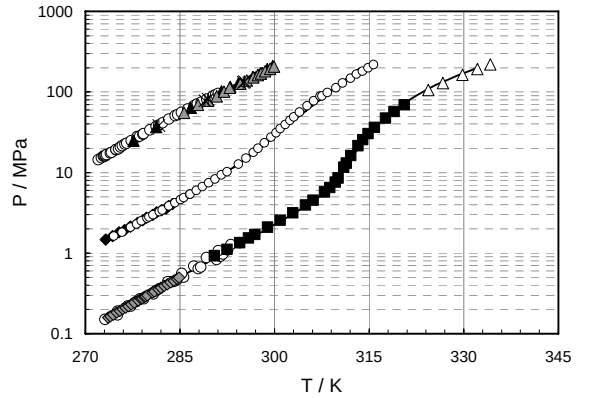

Figure 2 Experimental and predicted simple hydrate dissociation conditions. Experimental data for nitrogen hydrate from: (○) van Cleeff and Diepen [28], (▲) Marshall et al. [16], (▲) Sugahara et al. [29], and (✱) this work. Experimental data for krypton from: (◆) Maekawa [30], (○) and Sugahara et al. [31]. Experimental data for xenon from: (○) Maekawa [30], (■) Oghaki et al. [32], (◆) Shimada et al. [33], and (△) Sugahara et al. [31]. Black lines are the predictions of the developed model.

CONCLUSIONS

We have presented new experimental 3-phase H−L_W−V (Hydrate − Liquid Water− Vapour) equilibrium data for nitrogen and H−L_W−V (Hydrate − Liquid Water−Vapour) and H−L_W−L_{HC} (Hydrate − Liquid Water− Liquid Hydrocarbon) data for ethane and propane simple clathrate hydrates, generated by a reliable fixed-volume, isochoric, step-heating technique. These data in addition to the most reliable data from literature have been used to validate the predictive capabilities of a thermodynamic model presented in this work.

In the thermodynamic model presented here, the Valderrama modification of the Patel-Teja equation of state combined with NDD mixing rules is used to model the fluid phases. The hydrate are modelled by the solid solution theory of van der Waals and Platteeuw. Langmuir constants have been calculated by both Kihara potential as well as direct techniques. Good agreement between the model predictions and experimental data is observed, demonstrating the reliability and robustness of the developed model.

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