

# CLATHRATE HYDRATE EQUILIBRIA IN LIGHT OLEFINS AND MIXED METHANE – OLEFINS SYSTEMS

Antonin Chapoy\*, Ibrahim Alsiyabi, Jebraeel Gholinezhad, Rod Burgass and Bahman Tohidi

*Hydrates, Flow Assurance & Phase Equilibria, Institute of Petroleum Engineering, Heriot-Watt University, Edinburgh EH14 4AS, Scotland, UK*

## Abstract

*Light olefins such as ethylene and propylene are widely used in industry. When combined with water, they can form hydrates at correct thermodynamics conditions. In this paper, we report the results of new experimental measurements on the locus of incipient hydrate-liquid water-vapour curve for pure ethylene, propylene, ethylene + propylene, methane + propylene and ethylene + ethane (ongoing) systems.*

*Two different thermodynamic approaches were employed to investigate the phase behaviour of pure olefins and mixed systems: the Valderama-Patel-Teja (VPT) equation of state combined with the NDD mixing rules and the Cubic-Plus-Association equation of state. In all cases, the hydrate-forming conditions are modelled by the solid solution theory of van der Waals and Platteeuw. The parameters of the thermodynamic model were regressed using ethylene and propylene solubility in water and the model was used to predict the hydrate dissociation conditions of the various investigated systems. Predictions of the developed model are validated against independent experimental data and the data generated in this work. A good agreement between predictions and experimental data is observed, supporting the reliability of the developed model.*

*Keywords: Gas Hydrates; Ethylene; Propylene; Water; Methane; Experimental Measurements; Thermodynamic Model.*

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\* Corresponding author. Tel.: +44 (0) 131 451 3797; fax: +44 (0) 131 4513539.  
E-mail address: Antonin.Chapoy@pet.hw.ac.uk (A. Chapoy).

## 1. INTRODUCTION

Light olefins, and in particular ethylene, are the primary hydrocarbons used in the petrochemical industry [1]. These hydrocarbons are generally produced by steam cracking of hydrocarbons and are present in a variety of processes. Furthermore, ethylene is widely transported by pipelines all over the world from production points to petrochemical sites. During their production as well as in the other relevant processes, olefins can be in contact with traces of water or free water. Combined with the right thermodynamic conditions, the water vapour present in the gas phase may condense and form ice and / or gas hydrate. Formation of a free water phase may also lead to corrosion, two-phase flow problems, potential damage and blocked equipments. Accurate knowledge of hydrate phase equilibrium of olefins and mixed alkane-olefin systems is therefore crucial to avoid gas hydrate formation problems and to design/optimize hydrocarbon gas transmission lines and processing facilities.

In this communication, new experimental measurement of the locus of incipient hydrate-liquid water-vapour curve for pure ethylene are presented. In addition, new data of the locus of incipient hydrate-ice-vapour and hydrate-liquid water-vapour curves for pure propylene measured in the presence of a free water phase are reported. Hydrate dissociation conditions were also measured for methane + propylene, ethylene + propylene and ethane + ethylene binary systems.

The Cubic-Plus-Association equation of state (CPA-EoS) [2] and the Valderama-Patel-Teja (VPT) [3] equation of state combined with the NDD mixing rules [4] were employed to model the phase equilibria. The thermodynamic model is based on the uniformity of fugacity of each component throughout all the phases. For both approaches, the binary interaction parameters between ethylene and water and propylene and water were tuned using the literature solubility data. The hydrate-forming conditions were modelled by the solid solution theory of van der Waals and Platteeuw [5] as developed by Parrish and Prausnitz [6]. Langmuir constants were calculated using Kihara potential [7]. The single ethylene and propylene hydrate data along with literature data were used to tune the Kihara parameters. The model predictions were validated and compared with the new binary and ternary hydrate data as well as with the literature data.

## 2. EXPERIMENTAL SECTION

### 2.1. Materials

Ultra high purity grade methane, ethane, ethylene and propylene (99.995% pure) supplied by BOC were used. Deionised water was used in all tests. The synthetic binary systems used in this work were prepared gravimetrically in this laboratory; their compositions are given in Table 1.

### 2.2. Experimental Apparatus and Procedures

Dissociation point measurements were conducted using the isochoric step-heating method developed in this laboratory, which has previously been demonstrated as being considerably more reliable and repeatable than conventional continuous heating and/or visual techniques [8]. Figure 1 shows the apparatus used to determine the phase equilibrium conditions. The phase equilibrium is achieved in a cylindrical cell made of Hastelloy. The cell volume is about 80 cm<sup>3</sup> and it can be operated up to 40 MPa between 243 K and 323 K. A detailed description of the apparatus and test procedure can be found elsewhere [2].

## 3. PHASE EQUILIBRIA MODEL

A detailed description of the original thermodynamic model used in this work can be found elsewhere [2, 3]. In summary, the thermodynamic model based on the uniformity of fugacity of each component throughout all the phases is extended to model the equilibrium conditions. The CPA-EoS or the VPT-EoS are used to determine the component fugacities in fluid phases. The hydrate phase is modelled using the solid solution theory of van der Waals and Platteeuw as developed by Parrish and Prausnitz [7]. The Kihara model for spherical molecules is applied to calculate the potential function for compounds forming hydrate phases. More detail about hydrate modelling technique used in this work can be found elsewhere [1, 3]. The critical properties of components used in this work and the CPA parameters for water are given in Table 2 and Table 3, respectively.

## 4.4. RESULTS AND DISCUSSION

The experimental hydrate dissociation data for ethylene, propylene, methane + propylene and ethylene + propylene are given in Tables 4 to 7, respectively, and plotted in Figures 2

to 6. Experimental data for ethane + ethylene is presented in Table 8 and plotted in Figure 7.

VLE data from the literature were gathered for the ethylene – water system (Table 9) and for the propylene- water system (Table 10).

The binary interaction parameters (BIPs) between water and ethylene as well as between water and propylene were adjusted using the solubility data presented in Tables 8 and 9 through a Simplex algorithm using the objective function,  $OF$ , displayed in equation 1:

$$OF = \frac{1}{N} \sum_1^N \left| \frac{x_{exp} - x_{cal}}{x_{exp}} \right| \quad (1)$$

Where  $x$  is the solubility of the gas in water,  $N$  is the number of data points. BIPs for the VPT-EoS combined with the NDD mixing rules as well as those of CPA-EoS are given in Table 11 and Table 12.

The various isothermal  $P, x$  data sets from the literature for the ethylene–water are well represented with the VPT-EoS and NDD mixing rules or the CPA-EoS with the new BIPS parameters (Figures 8 and 9). The regressed models can also predict with good accuracy the solubility of propylene in water over a wide range of temperature and pressure conditions (Figures 10 and 11).

VLE equilibrium and bubble point data have also been gathered for the various non-polar systems, i.e. methane +ethylene, methane + propylene, ethane + ethylene, ethane + propylene, ethylene +propylene. The binary interaction parameters between these hydrocarbons were adjusted using the references mentioned in Table 13 through a Simplex algorithm using the objective function,  $OF$ , displayed in equation 2:

$$OF = \begin{cases} \frac{1}{N} \sum_1^N \left( \frac{p_{exp}^{Bubble} - p_{cal}^{Bubble}}{p_{exp}^{Bubble}} \right)^2 \\ or \\ \frac{1}{N} \sum_1^N \left[ \left( \frac{y_{exp} - y_{cal}}{y_{exp}} \right)^2 + \left( \frac{x_{exp} - x_{cal}}{x_{exp}} \right)^2 \right] \end{cases} \quad (2)$$

### ***Application of the model to hydrate modelling***

The hard-core radius,  $\alpha$ , of the Kihara potential parameter for ethylene and propylene was calculated from correlations given by Tee *et al.* [46]. This value was considered acceptable for hydrate modelling, given that predictions are not significantly affected by minor changes in the core radius.

The two remaining Kihara potential parameters for ethylene and propylene—the collision diameter “ $\sigma$ ” and the depth of the energy well “ $\epsilon$ ” were optimized using the new experimental hydrate dissociation data reported in Tables 3 and 4 as well as some of the literature data by using the method of Tohidi-Kalorazi [47]. For ethylene, 2 scenarios were considered: occupancy of the large cage of structure I and occupancy of the small and large cages of structure I. We have used the resulting model, as detailed above, to predict *H-L-V* equilibria for those systems investigated experimentally. Predictions are compared with experimental data in Figures 2 to 4. It can be seen that predictions are in good agreement with the experimental data, supporting the reliability of the thermodynamic model. It can also be noticed that predictions, particularly at high pressures, agree better with experimental data, if we assume that ethylene occupies both small and large cavities. Sugahara *et al.* (2000) [13] have shown using Raman scattering that, despite its large diameter, ethylene could occupy the small cages of structure I. The Kihara parameters for ethylene and propylene are given in the Table 14. As can be seen in Figure 2, the data of Reamer *et al.* (1952) [12] are particularly scattered and are not in agreement with the other data (about 0.5-1 MPa higher). It is also interesting to note that the ethylene hydrate locus displays a nice “S” shape (Figure 3) as the locus is not intersecting the liquid – liquid locus (as carbon dioxide, ethane or propylene, ethylene critical point is 282.4 K and 4.88 MPa). At low pressure and low temperature (below 4.88 MPa), the system is in equilibrium with a vapour rich ethylene phase) and at higher pressure the system is in equilibrium with a supercritical fluid (denser).

As seen in Figure 4, the hydrate locus of propylene is relatively narrow, the quadruple point (hydrate – vapour –liquid propylene –liquid water) of the system is estimated to be around 274.2 K and the system is far less stable than propane.

The developed models were also used to predict the hydrate stability conditions of the methane + propylene systems (Figure 5) and ethylene – propylene (Figure 6) and were

compared with the new measured data and the data measured by Ma et al. (2001) [14]. The predictions are in good agreement with the experimental data, demonstrating the reliability of the models used in this work.

## 5. CONCLUSIONS

In this work, two thermodynamic models using the well-proven Cubic-Plus-Association equation of state (CPA-EoS) or the Valderama-Patel-Teja (VPT) equation of state combined with the NDD mixing rules were employed to model the phase equilibria of ethylene and propylene systems in the presence of water. Literature solubility data were used to regress the parameters of the models.

Moreover, new experimental measurement of the locus of incipient hydrate-liquid water-vapour curve for pure ethylene, propylene, ethylene + propylene, methane + propylene and ethylene + ethane systems are presented. The predictions of the developed model are compared against independent experimental hydrate dissociation data and the data generated in this work. A good agreement between predictions and experimental data is observed, demonstrating the reliability of the developed models.

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**Table 1.** Composition of the synthetic mixtures used in the tests.

| <b>Comp.</b>                  | <b>Composition (mole%)</b> |              |              |              |
|-------------------------------|----------------------------|--------------|--------------|--------------|
|                               | <b>Mix 1</b>               | <b>Mix 2</b> | <b>Mix 3</b> | <b>Mix 4</b> |
| CH <sub>4</sub>               | Balance                    | Balance      | -            | -            |
| C <sub>2</sub> H <sub>6</sub> | -                          | -            | -            | Balance      |
| C <sub>2</sub> H <sub>4</sub> | -                          | 12(±0.3)     | Balance      | 10(±0.3)     |
| C <sub>3</sub> H <sub>6</sub> | 10 (±0.3)                  | -            | 10(±0.3)     | -            |
| Total                         | 100                        | 100          | 100          | 100          |

**Table 2.** Critical properties of pure compounds (Reid et al. [9])

| Compound                      | $p_c$ /MPa | $T_c$ /K | $\omega$ | $v_c$ /m <sup>3</sup> .kgmol <sup>-1</sup> |
|-------------------------------|------------|----------|----------|--|
| H <sub>2</sub> O              | 22.048     | 647.30   | 0.3442   | 0.056                                      |
| CH <sub>4</sub>               | 4.604      | 190.58   | 0.0108   | 0.0991                                     |
| C <sub>2</sub> H <sub>6</sub> | 4.880      | 305.42   | 0.09896  | 0.1479                                     |
| C <sub>2</sub> H <sub>4</sub> | 5.036      | 282.4    | 0.0850   | 0.1290                                     |
| C <sub>2</sub> H <sub>6</sub> | 4.620      | 365.0    | 0.148    | 0.181                                      |

**Table 3.** CPA Parameters for Water (Kontogeorgis et al. [10])

| $a_0/\text{MPa L}^2 \text{ mol}^{-2}$ | $b/\text{L mol}^{-1}$ | $c_1$  | $\varepsilon/\text{MPa L mol}^{-1}$ | $\beta$<br>( $\times 10^3$ ) |
|---------------------------------------|-----------------------|--------|-------------------------------------|------------------------------|
| 0.1228                                | 0.01452               | 0.6736 | 16.655                              | 69.2                         |

**Table 4.** Experimental hydrate dissociation points for ethylene.

| T/ K<br>( $\pm 0.1$ ) | P/ kPa<br>( $\pm 5$ ) | T/ K<br>( $\pm 0.1$ ) | P/ kPa<br>( $\pm 5$ ) |
|-----------------------|-----------------------|-----------------------|-----------------------|
| 276.15                | 772                   | 290.65                | 4957                  |
| 281.45                | 1434                  | 292.75                | 10301                 |
| 287.85                | 3213                  | 293.95                | 17885                 |
| 289.95                | 4440                  | 295.45                | 26131                 |

**Table 5.** Experimental hydrate dissociation points for propylene.

| T/ K<br>( $\pm 0.02$ ) | P/ kPa<br>( $\pm 5$ ) | T/ K<br>( $\pm 0.02$ ) | P/ kPa<br>( $\pm 5$ ) |
|------------------------|-----------------------|------------------------|-----------------------|
| 270.71                 | 432                   | 273.55                 | 520                   |
| 271.15                 | 437                   | 273.67                 | 538                   |
| 271.71                 | 445                   | 273.78                 | 550                   |
| 272.15                 | 452                   | 273.89                 | 563                   |
| 272.61                 | 462                   | 274.05                 | 585                   |
| 273.11                 | 472                   | 274.17                 | 601                   |
| 273.17                 | 475                   | 274.24                 | 610                   |
| 273.43                 | 507                   |                        |                       |

**Table 6.** Experimental hydrate dissociation points for 88 mole% methane + 12 mole% propylene.

| T/ K<br>( $\pm 0.1$ ) | P/ kPa<br>( $\pm 5$ ) | T/ K<br>( $\pm 0.1$ ) | P/ kPa<br>( $\pm 5$ ) |
|-----------------------|-----------------------|-----------------------|-----------------------|
| 274.15                | 918                   | 285.95                | 3434                  |
| 278.00                | 1380                  | 288.75                | 4848                  |
| 280.85                | 1906                  | 291.55                | 7205                  |
| 283.65                | 2599                  | 293.65                | 10208                 |



**Table 7.** Experimental hydrate dissociation points for 90 mole% ethylene + 10 mole% propylene.

| T/ K<br>( $\pm 0.1$ ) | P/ kPa<br>( $\pm 5$ ) |
|-----------------------|-----------------------|
| 279.45                | 1248                  |
| 287.3                 | 3427                  |
| 289.55                | 4750                  |
| 291.15                | 6364                  |
| 291.35                | 7695                  |
| 292.35                | 12466                 |
| 292.45                | 15237                 |
| 294.45                | 26241                 |

**Table 8.** Experimental hydrate dissociation points for 90 mole% ethane + 10 mole% ethylene.

| T/ K<br>( $\pm 0.1$ ) | P/ kPa<br>( $\pm 5$ ) |
|-----------------------|-----------------------|
| 275.35                | 634                   |
| 282.05                | 1407                  |
| 288.05                | 3447                  |
| 288.75                | 4254                  |

**Table 9.** Experimental high pressure VLE data for the ethylene – water systems.

| Reference                       | Type of data           | T / K         | P/ MPa   | Nbr Pts |
|---------------------------------|------------------------|---------------|----------|---------|
| Bradbury et al. (1951) [19]     | <i>PT<sub>x</sub></i>  | 308.1 -379.1  | 0.5-53.1 | 53      |
| Sidorov et al. (1952) [20]      | <i>PT<sub>y</sub></i>  | 323.15-373.15 | 5.1-25.3 | 27      |
| Tsiklis et al. (1958) [21]      | <i>PT<sub>xy</sub></i> | 469.15-565.15 | 5.1-17.9 | 45      |
| Davis and McKetta (1960) [22]   | <i>PT<sub>x</sub></i>  | 310.93-394.26 | 0.2-37.4 | 46      |
| Tsiklis et al. (1960) [23]      | <i>PT<sub>xy</sub></i> | 469.15-565.15 | 5.1-17.9 | 45      |
| Anthony and McKetta (1967) [24] | <i>PT<sub>x</sub></i>  | 310.93-410.93 | 1.4-34.5 | 48      |
| Sanchez and Lentz (1973) [25]   | <i>PT<sub>x</sub></i>  | 439.1-573.15  | 10-55    | 12      |

**Table 10.** Experimental high pressure VLE data for the propylene – water systems.

| Reference                         | Type of data | T / K           | P/ MPa  | Nbr Pts |
|-----------------------------------|--------------|-----------------|---------|---------|
| Azarnoosh and McKetta (1959) [26] | <i>PTx</i>   | 294.26 -379.6   | 0.1-3.4 | 107     |
| Li and McKetta (1963) [27]        | <i>PTxy</i>  | 310.93 – 410.84 | 0.3-33  | 104     |
| Sanchez and Lentz (1973) [25]     | <i>PTx</i>   | 439.1-573.15    | 10-55   | 12      |

**Table 11.** BIPs for the VPT-EoS and NDD mixing rules.

| System            | $k_{w-hc}$ | $L_{w-hc}^0$ | $L_{w-hc}^1 \times 10^4$ |
|-------------------|------------|--------------|--------------------------|
| Ethylene - Water  | -0.275     | -0.013       | 29.47                    |
| Propylene - Water | 0.500      | 1.462        | 27.35                    |

**Table 12.** BIPs for the CPA-EoS

| System            | $k_{w-hc}$           |
|-------------------|----------------------|
| Ethylene - Water  | $-65.731/T + 0.1483$ |
| Propylene - Water | $-46.446/T + 0.1051$ |

**Table 13.** BIPs for the VPT-EoS and SRK/CPA-EoS.

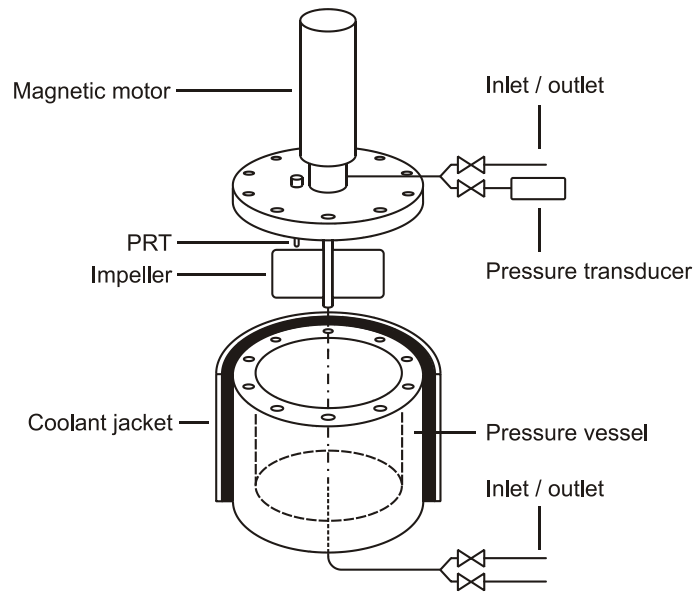
| System               | $k_{ij}$ |         | Sources      |
|----------------------|----------|---------|--------------|
|                      | VPT      | SRK/CPA |              |
| Methane – Ethylene   | 0.0286   | 0.0259  | [28-30]      |
| Methane – Propylene  | 0.0413   | 0.0344  | [31-34]      |
| Ethane – Ethylene    | 0.0151   | 0.0105  | [34-40]      |
| Ethane – Propylene   | 0.0219   | 0.0215  | [34, 41-43]  |
| Ethylene - Propylene | -0.0131  | -0.0122 | [41, 44, 45] |

**Table 14.** Optimized Kihara Parameters for ethylene and propylene ( $\alpha$  = Collision Diameter,  $\varepsilon$  = Depth of Energy Well,  $k$  = Boltzmann's Constant)

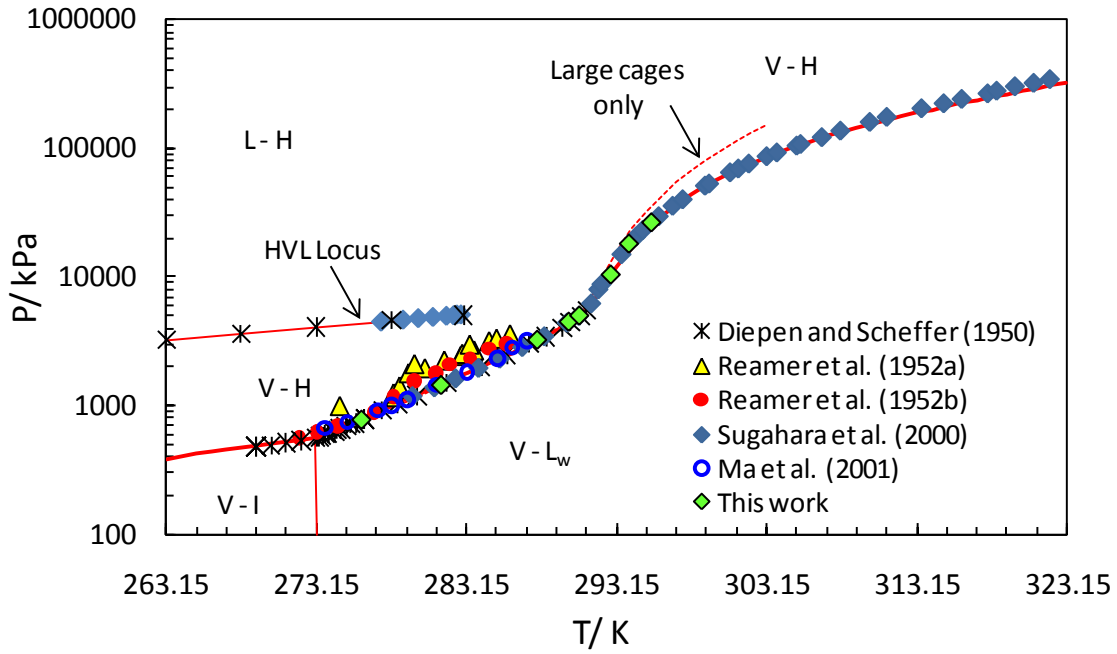
| Component | $\alpha / \text{\AA}$ | $\sigma^{*a} / \text{\AA}$ | $(\varepsilon / \kappa) / \text{K}$ |
|-----------|-----------------------|----------------------------|-------------------------------------|
| Ethylene  | 0.3894                | 3.350                      | 173                                 |
| Propylene | 0.5694                | 3.4315                     | 189                                 |

<sup>a</sup>  $\sigma^* = \sigma - 2\alpha$

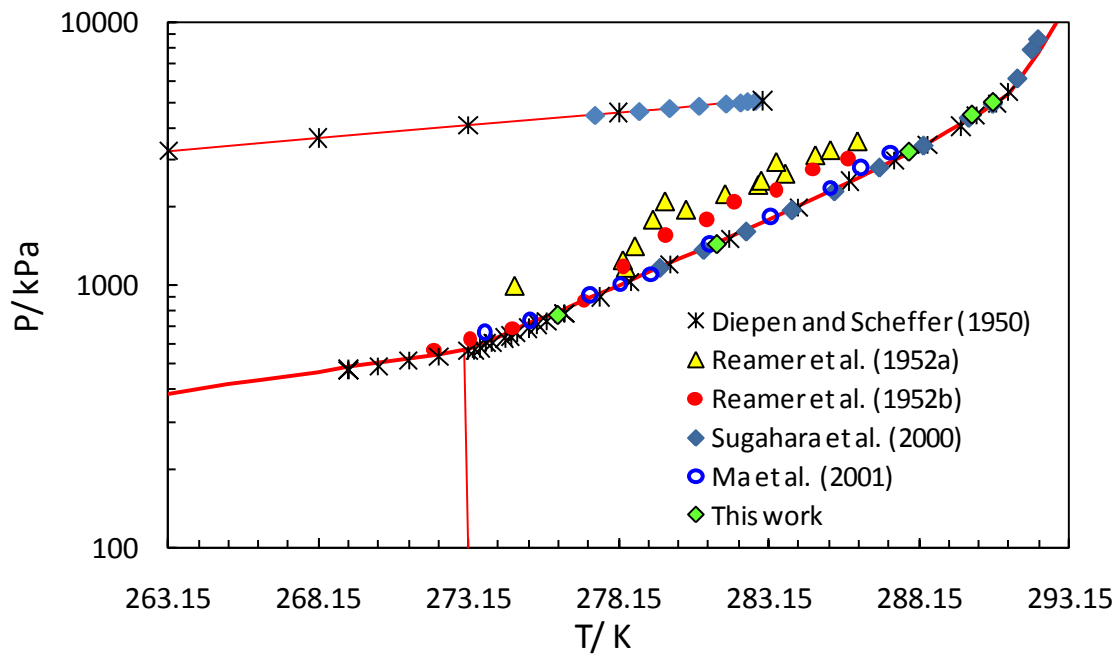




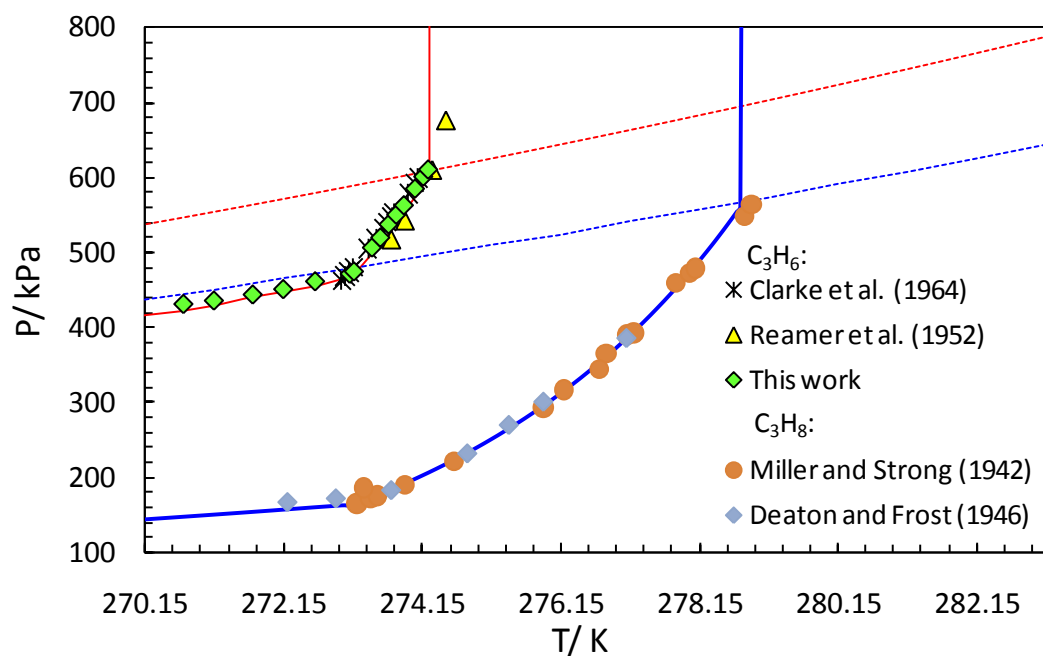
**Figure 1.** Schematic illustration of high-pressure rig



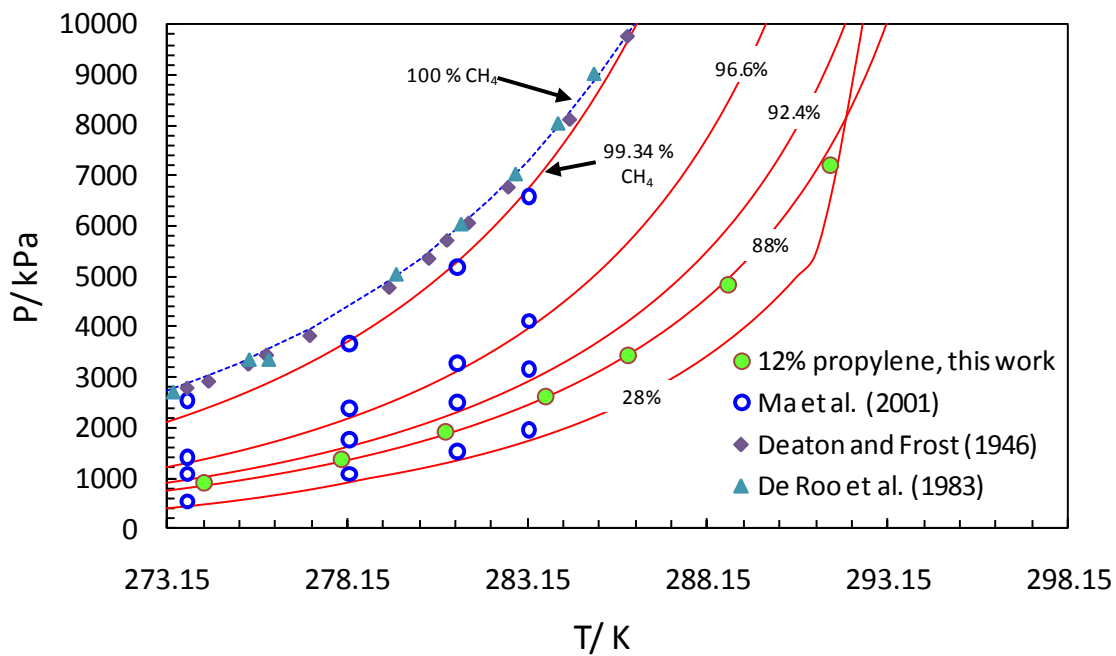
**Figure 2.** Experimental and predicted ethylene hydrate dissociation conditions.  $\blacklozenge$ : this work;  $\ast$ : data from Diepen and Scheffer (1950) [11];  $\blacktriangle$ : data from Reamer et al. (1952a) [12];  $\bullet$ : data from Reamer et al. (1952b) [12];  $\blacklozenge$ : data from Sugahara et al. (2000) [13];  $\bullet$ : data from Ma et al. (2001) [14]. Red curves: Predictions assuming small and large occupancy. Red dotted lines: Predictions assuming large cage occupancy only.



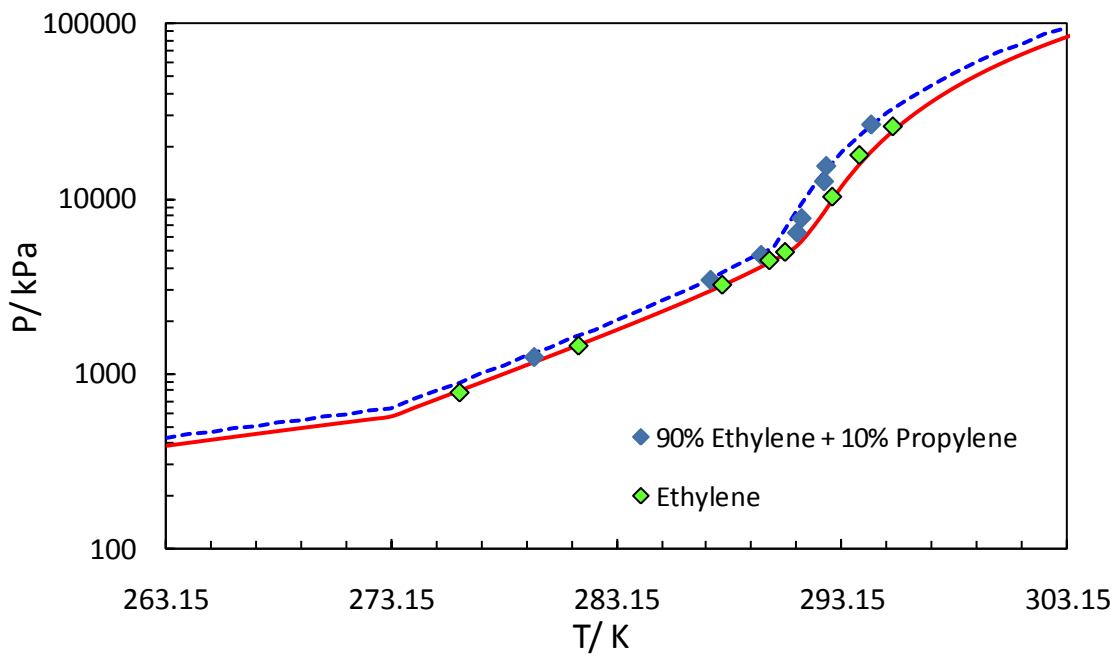
**Figure 3.** Experimental and predicted ethylene hydrate dissociation conditions. ◆: this work; ✱: data from Diepen and Scheffer (1950) [11]; ▲: data from Reamer et al. (1952a) [12]; ●: data from Reamer et al. (1952b) [12]; ◆: data from Sugahara et al. (2000) [13]; ○: data from Ma et al. (2001) [14]. Red curves: Predictions assuming small and large occupancy. Red dotted lines: Predictions assuming large cage occupancy only.



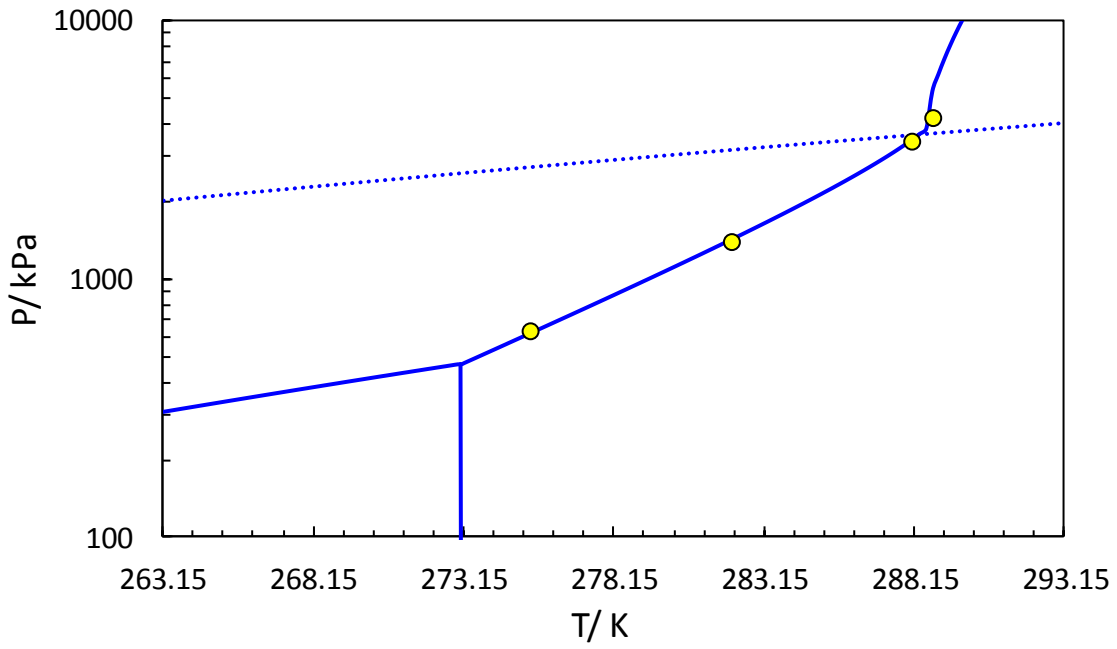
**Figure 4.** Experimental and predicted propylene and propane hydrate dissociation conditions. *Propylene*: ◆: this work; \*: data from Clarke et al. (1964) [15]; ▲: data from Reamer et al. (1952) [12]; *Propane*: ●: data from Miller and Strong (1942) [16]; ◆: data from Deaton and Frost (1946) [17].



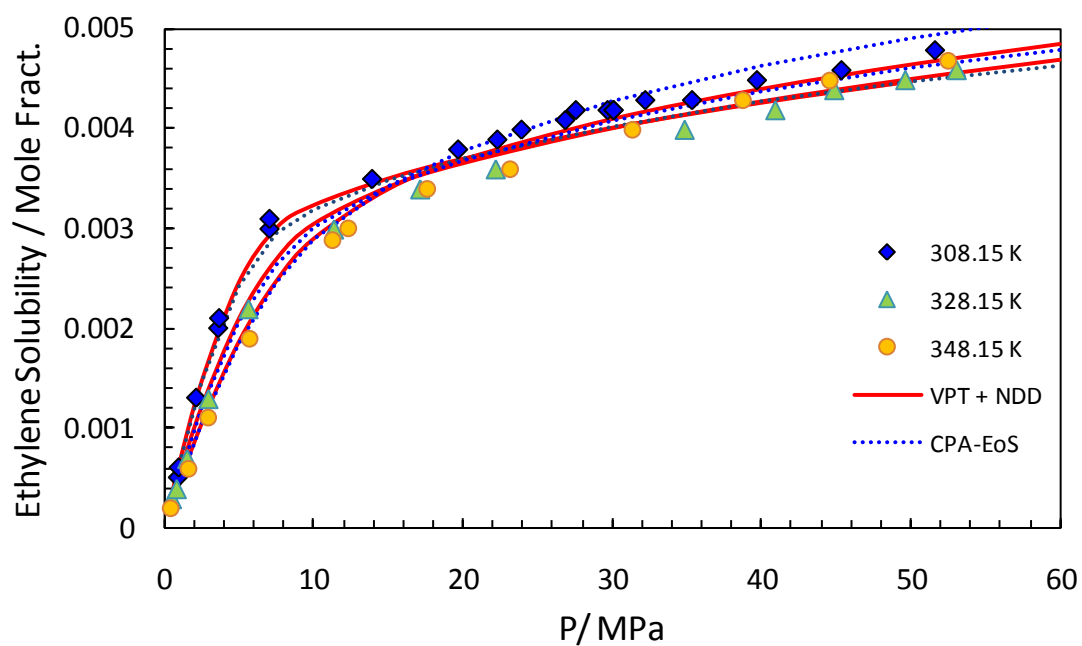
**Figure 5.** Experimental and predicted mixed methane + propylene hydrate dissociation conditions.  $\blacklozenge$ : this work;  $\circ$ : data from Ma et al. (2001) [14]. (Pure methane data:  $\blacklozenge$ : data from Deaton and Frost (1946) [17];  $\blacktriangle$ : data from de Roo et al. (1983) [18].



**Figure 6.** Experimental and predicted mixed ethylene + propylene hydrate dissociation conditions.  $\blacklozenge$ : Pure ethylene;  $\blacklozenge$ : 90mole% ethylene +10mole% propylene.

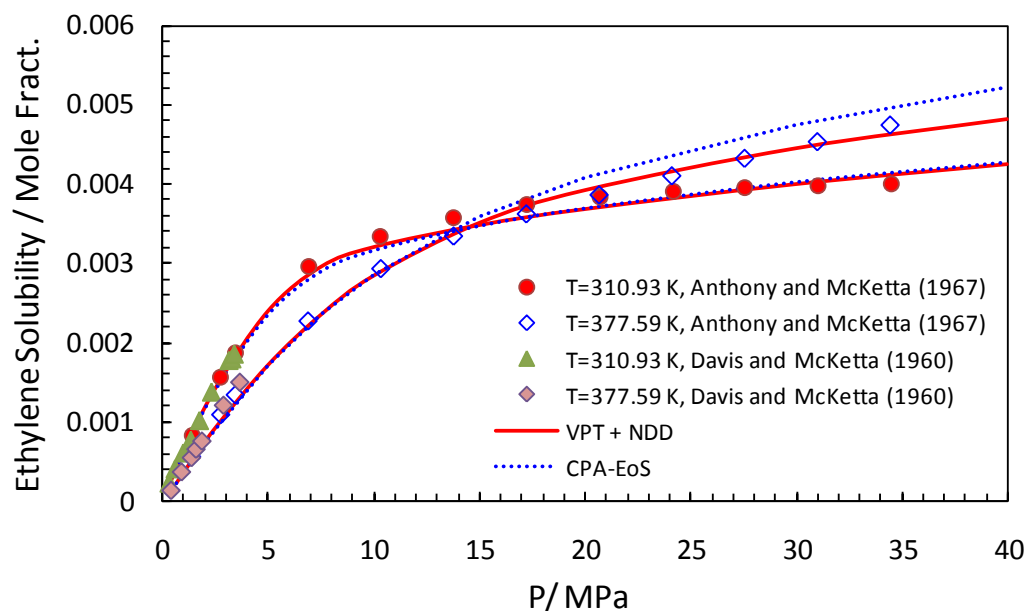


**Figure 7.** Experimental and predicted mixed ethane + ethylene hydrate dissociation conditions. ●: 90mole% ethane +10mole% ethylene.

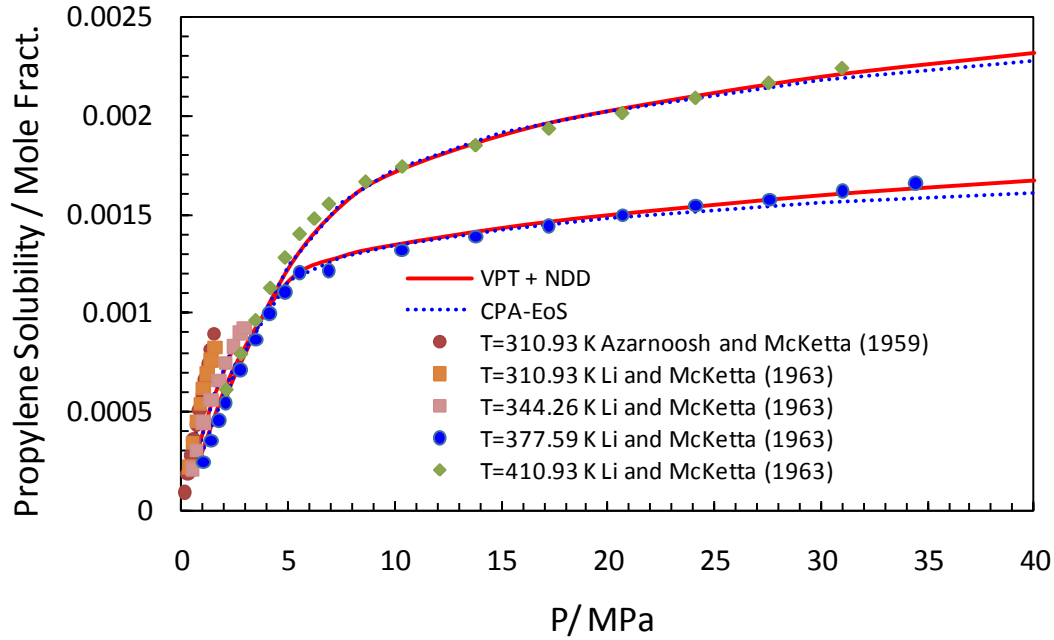


**Figure 8.** Experimental and calculated ethylene solubility in water.  $\blacklozenge$ :  $T=308.15$  K data from Bradbury et al. (1951) [19];  $\blacktriangle$ :  $T=328.15$  K data from Bradbury et al. (1951) [19];  $\bullet$ :  $T=348.15$  K data from Bradbury et al. (1951) [19]; Red lines: VPT-EoS+NDD model calculations; Blue dotted lines: CPA-EoS model calculations.

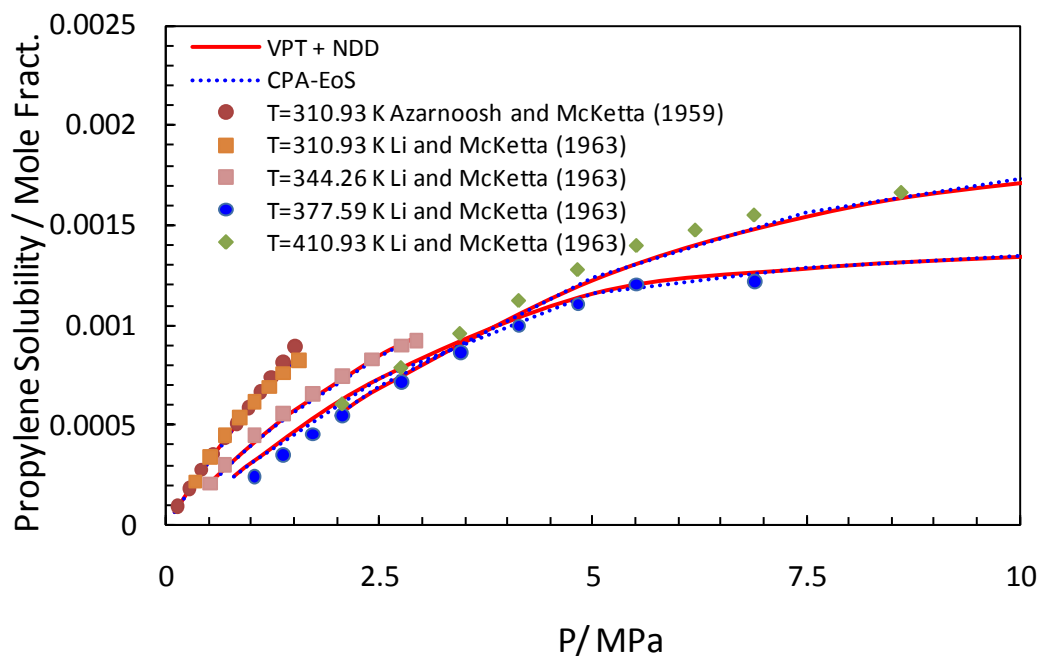




**Figure 9.** Experimental and calculated ethylene solubility in water.  $\blacktriangle$ : T=310.93 K data from Davis and McKetta (1960) [22];  $\blacklozenge$ : T=377.59 K data from Davis and McKetta (1960) [22];  $\bullet$ : T=310.93 K data from Anthony and McKetta (1967) [24];  $\blacklozenge$ : T=377.59 K data from Anthony and McKetta (1967) [24]; Red lines: VPT-EoS+NDD model calculations; Blue dotted lines: CPA-EoS model calculations.



**Figure 10.** Experimental and calculated propylene solubility in water. ●: T=310.93 K data from Azarnoosh and McKetta (1959) [26]; ■: T=310.93 K data from Li and McKetta (1963) [27]; ■: T=344.26 K data from Li and McKetta (1963) [27]; ●: T=377.59 K data from Li and McKetta (1963) [27]; ◆: T=410.93 K data from Li and McKetta (1963) [27]; Red lines: VPT-EoS+NDD model calculations; Blue dotted lines: CPA-EoS model calculations.



**Figure 11.** Experimental and calculated propylene solubility in water. ●: T=310.93 K data from Azarnoosh and McKetta (1959) [26]; ■: T=310.93 K data from Li and McKetta (1963) [27]; ■: T=344.26 K data from Li and McKetta (1963) [27]; ●: T=377.59 K data from Li and McKetta (1963) [27]; ◆: T=410.93 K data from Li and McKetta (1963) [27]; Red lines: VPT-EoS+NDD model calculations; Blue dotted lines: CPA-EoS model calculations.